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PORTABLE SPECTROMETRIC ANALYZER FOR
AIR POLLUTANTS

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Final Report

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PORTABLE SPECTROMETRIC ANALYZER FOR AIR POLLUTION

FINAL REPORT

David T. Williams

Introduction

The proposal upon which the research here summarized was based is dated 10/1/66. The research aims were stated in two parts: a) the development of a readily portable spectrometric equipment for direct field measurement of air pollutants, sufficiently sensitive to compete with current chemical methods, and in real time; b) to carry out a program of measurements of air pollutants in Jacksonville, Florida.

The accomplishments achieved during the period of the sponsorship are detailed in the following pages. Extensive use is made of the PhD thesis of R. N. Hager; much of the material is taken directly from that work, which was supported by the project. However this report is written strictly from the standpoint of the sponsor's interest in finding solutions to the problems of air pollution. For this reason, it is proper to review the background of work on air pollution as it is related to spectrometric measurement.

Problems of Air Pollution Control

When the program reported here was started, interest in air pollution control was high, as it is now. The ultimate objective of air pollution control was quite clear: to work out a system of controls that would reduce the pollution level in cities to acceptable concentrations. Now

this was to be done, exactly, was not altogether clear in 1966. For example, it was generally agreed that measurement of air pollution levels ought to be made. But what pollutants? Continuously, or only during periods of high pollution levels? Routinely, or only on complaint of citizens? Further, the question of what to do with the pollution measurements was not clear. Obviously if a pollution source is reported by citizens, it would be the function of the air pollution control agency in the city to do something about it. What could it do? Clearly, it would have to enforce a law, if one were on the books. Strictly speaking, it could only gather data which would then be used as evidence in a legal action--or possibly as pressure to persuade the owners of the offending pollution source to install suitable air-cleaning equipment.

Even at best, the duties of the air pollution control agency were and are not always clear-cut. Thus suppose a pollution source is a factory employing many citizens. Is it the function of the agency to force the company to cease polluting the air, even at the risk of causing it to shut down? Or suppose the offender is a municipal power plant burning cheap fuel. Is the control agency to force the use of sulfur-free fuel, even if the cost of the power is thereby forced upward? Finally, the predictable intricacies of law enforcement are always a complication. Thus, should pollution sources be checked out at night or during weather periods when pollutants rise immediately into the atmosphere and do not therefore trigger complaints? And what kind of field data are likely to constitute effective evidence in court? How can one, for example, obtain data clearly tracing measured pollution levels to a particular source?

Answers to these questions are not always known; yet the instrumenta-

tion that may be most useful may often be dictated by the answers. Thus if a law is on the books forbidding the use of high-sulfur fuel, effective enforcement may hinge on whether there is also a law, and instrumentation, and provision for maintenance of that instrumentation in the stacks of all companies burning fuel subject to the law. Otherwise there is a problem of identifying the source of high-sulfur plumes, or proving that the company did in fact burn fuel of illegal sulfur content. Many subterfuges are to be anticipated in this connection, such as using low-sulfur fuels only during the day, or only on days when a temperature inversion holds the plumes close to the ground. In such case, instrumentation and its use must be designed for application to a kind of guerilla warfare game, where the opponents are the polluting sources and the control agency.

In 1966, and to much the same extent in 1970, it appears to us that prime requirements for instrumentation to be used by a good air pollution control agency would include a) an instrument that can detect and measure all, or at least most, of the air pollutants likely to be encountered; b) an instrument capable of detecting any pollutant, even those not usually encountered. It would be desirable further that the instrument or instruments should be readily portable, simple to use, and inexpensive. It would be a great convenience if the instruments used could operate unattended for extended periods, if desired. Finally, the services of highly trained operators should not be required.

These considerations were continually in our minds. They entered into decisions as to direction of the development program during the period 1967-70 when the program was active. And the final results are therefore substantially colored by the experience in the field gained during the three years of the contract.

The Spectrometer in Air Pollution Detection

It was recognized a priori that air pollutants should be detectable spectrometrically. A light beam of intensity I_0 would be projected down a range through a path length L ; it would be absorbed by the pollutant present in concentration c ; and the intensity I received at the end of the path would be given by

$$I = I_0 e^{-\mu c L}$$

Here μ is the absorption coefficient, unique for the wavelength and pollutant gas. In view of the fact that the concentrations c that are to be measured are extremely small, it was originally presumed that the path length L would have to be very large--of the order of a few hundred feet. For that reason, the system in which spectrometric determinations were to be made of pollutant concentration, was visualized as a number of ranges radiating outward from a central station, each terminated by a suitable mirror, or corner reflector. In this manner L would be twice the distance, spectrometer-to-mirror; and the range could be built so as to maintain a continuous survey of the pollution in the city center.

The instrumentation normally used in spectrometric measurements includes a spectrometer with source and receiver, in order to separate different wavelengths in the beam. A proper measurement would involve some kind of scanning technique so that I could be measured successively in regions where μ changes from a maximum to 0. If I_0 should change during the scanning period, from whatever cause, the precision of the determination of concentration could be no greater than the precision with which the source strength could be maintained constant. This limitation in itself would tend to limit the concentrations detectable to rather

high concentrations except where L is large.

Unfortunately, a light beam in the open seems to be subject to random fluctuations in intensity with time, due presumably to small gradients in refractive index due to temperature inhomogeneities, wind turbulence, etc. The fluctuations, in any case, completely mask changes in intensity with wavelength as the spectrum is scanned, when the scanning process is slow. For this reason, it was decided at an early stage to institute a sinusoidal oscillation of one of the spectrometer slits--providing a small scan that would hopefully be rapid enough to show up changes with wavelength during times short compared with the characteristic times of the air turbulence. The sinusoidal oscillation of the slit would produce a harmonic variation of wavelength. The signal would then have an AC component of known frequency and wavelength, in the event the amplitude should bracket an absorption minimum. This AC signal could then be selectively amplified by familiar electronic techniques, greatly increasing the signal-to-noise ratio. Furthermore, the signal would be proportional to the difference between I_0 and I , if the light source were chosen so that I_0 was nearly constant within the amplitude of the wavelength variation. Furthermore, if the product μcL were small, the difference $I_0 - I$ divided by I_0 , or by the constant DC component of the signal, would be quite independent of any possible fluctuations, fast or slow, of the light source intensity. And in fact, the measurement thus made should be strictly proportional to μcL by virtue of its small magnitude.

At the time of the initiation of the project, the use of multiple slits in place of a single one, at the position of the exit slit of the spectrometer, was favored. These multiple slits were spaced to conform to the spectrum of one of the pollutants being measured. The arrangement

is known under the name of the Molecular Correlation Spectrometer. It was thought at the time to provide some reduction in the interference anticipated due to other pollutants in the same air, which might have spectra interfering with that of the one being measured (see Ref. 1).

This was roughly the situation when the program was initiated.

Historical Review

The first project undertaken in the development program was the design and fabrication of a suitable electronic system. Initially the apparatus used had consisted of a $\frac{1}{2}$ -meter Fastie-Ebert spectrometer with a motor-driven exit mask replacing the exit slit. The light source--a deuterium arc--with power supply; the power supply for the receiver tube; a phase lock-in amplifier using vacuum tubes; a power supply for that device; and a recorder, standing 6 ft high from the floor, altogether made up a truck full of electronic equipment which required about an hour to load, and another hour to unload, when three men were available. The set-up time took another hour.

The miniaturization of the amplifier, together with a more discriminating selection of spectrometer and recorder produced a system that consisted of three units of which only one was not readily portable in one hand. The assembly consisting of a $\frac{1}{4}$ -meter spectrometer, a folded light path in an absorption cell, and light source with power supply was light enough to carry single-handed, but awkward enough to normally require two men. The electronic box, and the recorder were light and easily handled. All three components could be loaded into a station wagon, used in transit, and off-loaded without significant change in calibration as long as nothing was dropped or jolted.

Incidental to the miniaturization of the electronic circuitry was the discovery that the amplification of the AC part of the signal, and the subsequent division of this part by the averaged DC portion of the same signal, was equivalent to taking a derivative of the normalized spectrometer output with respect to wavelength. Also incidental to this part of the development was the discovery that the system as designed was extraordinarily sensitive to the presence of absorbing pollutant gases. It became quite evident, in fact, that it would not be necessary, or even desirable, to set up a permanent range for measurement of air pollutant concentration. Most of the gases with spectra lying within the range of the deuterium arc output could be detected and measured down to parts per 100 million or less with optical paths no more than 10 meters long. Such path lengths can be easily provided in cells small enough to fit into a station wagon, and light enough to be packaged in a portable instrument.

Finally as experience was accumulated in the measurement of various gas concentrations, it was discovered that the ammonia and sulfur dioxide bands are directly superposed in the spectral region between 210 and 200 millimicrons. This came as something of a shock in view of the fact that the molecular correlation method was supposed to greatly reduce or eliminate such interference. When it was realized that there was no conceivable way of eliminating this important interference effect by use of the correlation method, the question immediately became pertinent, why use the method? Accordingly the mask was replaced by a single oscillating slit. As a result, it was no longer necessary to provide for different masks for different gases. Instead, the entire range of wavelength available to the spectrometer could be scanned without change in equipment. Each

line of each pollutant absorbing gas was then detected as the derivative of the intensity-wavelength spectrum. In particular, by reason of the detailed design of the electronic set-up, the second derivative was the one recorded. The system, in short, became a second derivative (d^2) spectrometer.

The instrument in the form of a system made up of the three packages indicated, was at this point subjected to a careful and fundamental theoretical analysis presented below. Also the characteristics of the system were explored in two applications: a) the detection of ammonia in blood, and b) the recording of multiple concentrations of pollutant gases in Jacksonville. These studies, reported below, led to the conclusion that the d^2 spectrometer was a new and important type of spectrometric equipment. Even though the principles of the device were previously known, no exploitation of the idea has thus far been brought to practice. The sensitivity far exceeds that of any other spectrometer previously known. Accordingly steps were taken to take out design patents, have them released by HEW to the University of Florida, and arrange for manufacture of the d^2 spectrometer by a company "Spectrometrics of Florida", with interested backing by ABA Industries of St. Petersburg, under license from the University. Since termination of support by HEW, the redesign of the spectrometer for production has gone forward by Spectrometrics. The prototype was on display in Washington D.C. at a meeting of the NAPCA from Dec. 6 to 11, 1970.

The part of the original proposal relating to the setting up of a system of long absorption paths over open ranges in the city was dropped after some considerable thought. The reasoning went as follows:

a) The necessity of long paths for use of the spectrometric method of pollutant measurement was shown to exist no longer. If, nevertheless,

such ranges were to be set up, it should be on the basis that such a system has inherent advantages, per se.

b) It is conceivable that in some cities, the network of fixed ranges might be desirable. It was hard to become convinced that such would normally be the case, and certainly not in Jacksonville. In that city, unattended equipment was found to be often vulnerable to malicious mischief. It was hard to visualize a location where the type of range visualized would be easily set up and protected from damage. Furthermore the levels of pollution were critically dependent on the weather and wind direction. A continuing record of sulfur dioxide concentration, for example, might show a day or two per month on which significant concentrations of that pollutant were recorded.

c) A station wagon or van carrying instruments capable of recording concentrations of many pollutants, at various locations, and movable at will, was considered to be a much more attractive and useful type of system in the air pollution control program in Jacksonville than the fixed system originally envisioned. The d^2 spectrometer would make such a movable detection station feasible for the first time, with the transportation requirement met by any vehicle from a panel truck or van to a light station wagon, or possibly even a touring car.

Accordingly all the effort available was put into gaining experience with the d^2 spectrometer otherwise than in the fixed long-path system.

1. THEORY OF THE DERIVATIVE SPECTROMETER

The derivative spectrometer was subjected to a careful theoretical analysis, as a part of the doctoral dissertation of R. N. Mager. This analysis, which is also described in Ref. 2, is presented below.

Consider initially a direct conventional spectrometer. Let $I_0(\lambda)$ be a spectral distribution entering the spectrometer, and let $I(\lambda)$ be the measured spectral intensity. If now λ is permitted to change by a small increment $\Delta\lambda$, the intensity I may be expressed as a function of the increment $\Delta\lambda$ in the vicinity of λ_0 by use of the Taylor series expansion:

$$I(\lambda) = I(\lambda_0) + I^{(1)}(\lambda_0)\Delta\lambda + \frac{1}{2!} I^{(2)}(\lambda_0)\Delta\lambda^2 + \dots + \frac{1}{n!} I^{(n)}(\lambda_0)\Delta\lambda^n + \dots \quad (1)$$

where the notation $I^{(n)}(\lambda_0)$ means the n^{th} derivative of $I(\lambda)$ with respect to λ , evaluated at λ_0 .

Suppose now that the spectrometer is modified so that the wavelength detected varies sinusoidally with time about the wavelength λ_0 . That is, $\Delta\lambda = a \sin(\omega t)$. In the present instrument, the exit slit, or entrance slit, oscillates at a frequency ω so that the amplitude is A , in millimeters. Then $a = A(d\lambda/dx)$, in angstroms, where $d\lambda/dx$ is the reciprocal of the spatial dispersion, in angstroms per millimeter. When this expression for the wavelength is set into Equ. 1, the result is an expression for I as a function of time:

$$I(\lambda_0, t) = I(\lambda_0) + I^{(1)}(\lambda_0)a \sin \omega t + \frac{1}{2!} I^{(2)}(\lambda_0)a^2 \sin^2 \omega t + \dots + \frac{1}{n!} I^{(n)}(\lambda_0)a^n \sin^n \omega t \quad (2)$$

The time functions that appear in the various terms of this series can be expressed in terms of multiple angle sine or cosine functions, by use of relationships to be found in Ref. 3:

$$\sin^{2n}(\omega t) = \frac{1}{2^{2n}} \left\{ \sum_{k=0}^{n-1} (-1)^{n-k} 2 \binom{2n}{k} \cos 2(n-k)\omega t + \binom{2n}{n} \right\}$$

$$\sin^{2n-1}(\omega t) = \frac{1}{2^{2n-2}} \sum_{k=0}^{n-1} (-1)^{n+k-1} \binom{2n-1}{k} \sin(2n-2k-1)\omega t$$

The notation $\binom{p}{q}$ is the binomial coefficient defined as $\frac{p!}{q!(p-q)!}$

Clearly the even powers become each a series containing cosine functions of even multiple angles from $2\omega t$ to $2n\omega t$, and the odd powers become a series of sine functions of odd multiple angles from ωt to $(2n-1)\omega t$.

The relations for $\sin^n(\omega t)$ when substituted into Eq. (2.2) yield

$$\begin{aligned} I(\lambda_0, t) = & I(\lambda_0) \\ & + \sum_{n=1}^{\infty} \left\{ \frac{a^{2n-1} I^{(2n-1)}(\lambda_0)}{(2n-1)! 2^{2n-2}} \sum_{k=0}^{n-1} (-1)^{n+k-1} \binom{2n-1}{k} \sin(2n-2k-1)\omega t \right\} \\ & + \sum_{n=1}^{\infty} \left\{ \frac{a^{2n} I^{(2n)}(\lambda_0)}{(2n)! 2^{2n}} \left[\sum_{k=0}^{n-1} 2 (-1)^{n-k} \binom{2n}{k} \cos 2(n-k)\omega t + \binom{2n}{n} \right] \right\} \end{aligned} \quad (3)$$

The coefficients of the terms in the various frequencies ω , 2ω , 3ω , etc., can be obtained by examination of Eq. 3 as follows:

The constant term is

$$\sum_{n=0}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)}}{2^n! 2^{2n}} \binom{2n}{n} = \sum_{n=0}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)}}{2^{2n} (n!)^2}$$

The coefficient of the $\cos 2m\omega t$ term is found by summing all terms for which $n-k = m$; that is, $k = n-m$. The finite sum reduces to a single term, namely that for which $k = n-m$, for each value of n in the infinite series $\geq m$.

The cosine terms therefore take the form

$$\left\{ \sum_{n=m}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)}}{2^n! 2^{2n}} (-1)^m 2 \binom{2n}{n-m} \right\} \cos 2m\omega t$$

or

$$\left\{ \sum_{n=m}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)} (-1)^m}{2^{2n-1} (n+m)! (n-m)!} \right\} \cos 2m\omega t.$$

Likewise the sine terms from Eq. (3) become

$$\left\{ \sum_{n=m}^{\infty} \frac{a^{2n-1} I(\lambda_0)^{(2n-1)}}{(2n-1)! 2^{2n-2}} (-1)^{2n-m-1} \binom{2n-1}{n-m} \right\} \sin(2m-1)\omega t$$

or

$$\left\{ \sum_{n=m}^{\infty} \frac{a^{2n-1} I(\lambda_0)^{(2n-1)}}{2^{2n-2} (n+m-1)! (n-m)!} \right\} \sin(2m-1)\omega t$$

Combining these results, Eq. 3 can be written

$$\begin{aligned} I(\lambda_0, t) = & \sum_{n=0}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)}}{2^{2n} (n!)^2} \\ & + \sum_{m=1}^{\infty} \left\{ \sin[(2m-1)\omega t] \sum_{n=m}^{\infty} \frac{a^{2n-1} I(\lambda_0)^{(2n-1)} (-1)^{m+1}}{2^{2n-2} (n+m-1)! (n-m)!} \right. \\ & \left. + \cos(2m\omega t) \sum_{n=m}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)} (-1)^m}{2^{2n-1} (n+m)! (n-m)!} \right\} \quad (4) \end{aligned}$$

Equation 4 represents the intensity of radiation reaching the detector as a function of time and λ_0 , and also the detector signal, if it is linear with the intensity. The first sum is the dc component of the signal, and the other two sums represent the ac component, expanded into the fundamental frequencies. Each of these components of any chosen frequency can be readily amplified selectively by use of well-known electronic circuitry to produce an output which is proportional to the content of the chosen frequency in the detector signal.

Fourier Transform of the d^m Signal

If $I_t(\lambda')$ represents the true variation with wavelength λ' of the light analyzed in the spectrometer, the actual output of the device is not $I_t(\lambda')$, but rather that function as modified by the slit function $S(\lambda - \lambda')$ of the spectrometer. Thus a monochromatic source illuminating the entrance slit would produce an image of the entrance slit at the exit slit. As the wavelength is changed, this image sweeps across the exit slit, and the image as recorded as a function of wavelength would vary linearly from 0 where the image just begins to come through the exit slit, to a peak when slit and image are in register, and then back to 0 again linearly, as the image goes out of register again. The slit function $S(\lambda - \lambda')$ is then such a function that the spectrometer output

$$I(\lambda) = \int_{-\infty}^{+\infty} I_t(\lambda') S(\lambda - \lambda') d\lambda' \quad (5)$$

Strictly speaking, S is a function equal to 1 within a region about λ just as wide as the exit slit divided by the dispersion $dx/d\lambda$. It therefore follows that $I(\lambda)$ is simply equal to the total portion of the true signal $I_t(\lambda)$ that is transmitted through the exit slit, after having illuminated the entrance slit, when the spectrometer is set at λ . The expression (5) is a "convolution integral."

Consider the Fourier transformation $I(z)$ of $I(\lambda)$ defined by

$$I(\lambda) = \int_{-\infty}^{+\infty} I(z) e^{-2\pi i \lambda z} dz$$

Clearly

$$\frac{d^r I(\lambda)}{d\lambda^r} = \int_{-\infty}^{+\infty} (-2\pi i z)^r I(z) e^{-2\pi i \lambda z} dz$$

It is a property of convolution integrals like Eq. 5 that

$$\overline{I}(z) = \overline{I_t}(z) \overline{S}(z)$$

Therefore

$$I^{(r)}(z) = \overline{I_t}(z) \overline{S}(z) (-2\pi i a z)^r$$

Referring now to Eq. 4, we define

$$\begin{aligned} \sum_0(\lambda_0) &= \sum_{n=0}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)}}{2^{2n} (n!)^2} \\ \sum_{2m-1}(\lambda_0) &= \sum_{n=m}^{\infty} \frac{a^{2n-1} I(\lambda_0)^{(2n-1)} (-1)^{m+1}}{2^{2n-2} (n+m-1)! (n-m)!} \\ \sum_{2m}(\lambda_0) &= \sum_{n=m}^{\infty} \frac{a^{2n} I(\lambda_0)^{(2n)} (-1)^m}{2^{2n-1} (n+m)! (n-m)!} \end{aligned}$$

The signals generated in the spectrometer will involve these sums; the Fourier transforms of the signals will involve the slit function transforms as well. Thus

$$\overline{\sum_0}(z) = \sum_{n=0}^{\infty} \frac{a^{2n} \overline{I_t}(z) \overline{S}(z) (-2\pi i z)^{2n}}{2^{2n} (n!)^2}$$

Now the defining equation for the integer Bessel function is

$$J_n(x) = \sum_{r=0}^{\infty} \frac{(-1)^r (x/r)^{n+2r}}{r! (n+r)!}$$

so that

$$\begin{aligned} \overline{\sum_0}(z) &= \overline{I_t}(z) \overline{S}(z) \sum_{n=0}^{\infty} \frac{(-i)^{2n} \left(\frac{2\pi a z}{2}\right)^{2n}}{(n!)^2} \\ &= \overline{I_t}(z) \overline{S}(z) J_0(2\pi a z) \end{aligned}$$

Also

$$\sum_{2m-1} \overline{I(z)} = \overline{I_t(z)} \overline{S(z)} \sum_{n=m}^{\infty} z \left(\frac{-2\pi i a z}{2} \right)^{2n-1} \frac{(-1)^{n+1}}{(n+m-1)!(n+m)!}$$

If we set $p = n - m$, and sum from $p = 0$ to $p = \infty$,

$$\begin{aligned} \sum_{2m-1} \overline{I(z)} &= \overline{I_t(z)} \overline{S(z)} \sum_{p=0}^{\infty} \frac{(-i\pi a z)^{2p+2m-1} (-1)^{m+1}}{p! (p+2m-1)!} \\ &= \overline{I_t(z)} \overline{S(z)} \sum_{p=0}^{\infty} \frac{2i(-1)^{2m+1} (\pi a z)^{2p+2m-1} (-1)^{m+1}}{p! (p+2m-1)!} \\ &= \overline{I_t(z)} \overline{S(z)} (-2i) J_{2m-1}(2\pi a z) \end{aligned}$$

A similar manipulation yields

$$\begin{aligned} \sum_{2m} \overline{I(z)} &= \overline{I_t(z)} \overline{S(z)} \sum_{p=0}^{\infty} 2(-i\pi a z)^{2p+2m} (-1)^m \\ &= \overline{I_t(z)} \overline{S(z)} 2 J_{2m}(2\pi a z) \end{aligned}$$

These results may be generalized to give

$$\sum \overline{I(z)} = C_m \overline{I_t(z)} \overline{S(z)} J_m(2\pi a z)$$

where

$$C_m = 1 \quad \text{for } m=0$$

$$-2i \quad 1, 3, \dots$$

$$+2 \quad 2, 4, \dots$$

It might be noticed in passing that an approximation for the m th derivative of I can be readily observed. Thus, suppose one approximate the Bessel's function by the first term only. Then for $dI(\lambda)/d\lambda$ we have

$$\frac{d\overline{I(z)}}{d\lambda} = \overline{I^{(1)}(z)} = \overline{I_t(z)} \overline{S(z)} (-2\pi i z)$$

If the first term is used to represent the entire Bessel's function,

$$J_1(2\pi az) \cong J_1^f(2\pi az) = \pi az$$

so that

$$\frac{d}{d\lambda} I(\lambda) = -\frac{2i}{a} \int \overline{I_t(z)} \overline{S(z)} J_1^f(2\pi az) e^{-2\pi iz\lambda} dz$$

The treatment can be generalized to yield

$$\frac{d^m}{d\lambda^m} I(\lambda) = \left(-\frac{2i}{a}\right)^m m! \int_{-\infty}^{+\infty} \overline{I_t(z)} \overline{S(z)} J_m^f(2\pi az) e^{-2\pi iz\lambda} dz \quad (8)$$

Now if the range within which the integrand of (8) is different from 0 is small, $J_m^f(2\pi az)$ is an acceptable approximation for $J_m(2\pi az)$.

The condition can always be met in principle by making the amplitude a small.

The usually accepted expression for $S(z)$ is (Ref. 4)

$$\overline{S(z)} = \text{sinc}^2(bz) = \left[\frac{\sin(\pi bz)}{\pi bz} \right]^2$$

where b is the spectrometer slit width.

Ref. 2 exhibits comparisons between values for Bessel's functions and the first-term approximation. Reprints of the reference are submitted with this report.

Exact Expression for Signal Output

Reference 2, referred to above, presents the exact expression for signal output in satisfactory detail: It is readily written down, once the inverse transforms of the Bessel functions are known. Thus suppose the Bessel functions are Fourier transforms of functions $f_m(\lambda)$, say,

whose nature is at this point not further specified. That is,

$$f_m(\lambda) = \int_{-\infty}^{+\infty} J_m(2\pi a z) e^{-2\pi i \lambda z} dz$$

It follows at once that the convolution written

$$\Sigma_0(\lambda_0) = I_e(\lambda) * S(\lambda) * f_0(\lambda)$$

has the transform

$$\Sigma_0(z) = \overline{I_e}(z) \overline{S}(z) J_0(2\pi a z)$$

Similar expressions are valid for the functions $\Sigma_{2m-1}(\lambda_0)$ and $\Sigma_{2m}(\lambda_0)$.

The functions of which the Bessel functions are Fourier transforms are known (Ref. 5). They are

$$f_m(\lambda) = \frac{2 T_m(\lambda/a)}{\pi (a^2 - \lambda^2)^{1/2}}$$

where T_m is the Chebyshev polynomial of the first kind. That is

$$\begin{aligned} \Sigma_0(\lambda_0) &= I_e(\lambda) * S(\lambda) * \frac{1}{\pi (a^2 - \lambda^2)^{1/2}}, \quad 0 < \lambda < a \\ \Sigma_m(\lambda_0) &= I_e(\lambda) * S(\lambda) * \frac{(-1)^c 2 T_m(\lambda/a)}{\pi (a^2 - \lambda^2)^{1/2}}, \quad 0 < \lambda < a \end{aligned}$$

where $c = m/2$ for even m , $m/2 + \frac{1}{2}$ for m odd. For $\lambda > a$, the Chebyshev polynomials vanish.

Fig. 1, taken from Ref. 2, shows the functions $T_m(\lambda/a)/(a^2 - \lambda^2)^{1/2}$ for $m = 0, 1$ and 2 . The instrument function $S'(\lambda)$ for the derivative spectrometer is then the convolution of the slit function $S(\lambda)$ of the conventional spectrometer with the function $f_m(\lambda)$:

$$S'(\lambda) = \frac{1}{\pi} (-1)^c S(\lambda) * T_m(\lambda/a) (a^2 - \lambda^2)^{-1/2} \quad (9)$$

where $c = m/2$ for m even, $m/2 + \frac{1}{2}$ for m odd.

The output signals of the derivative spectrometer can be written in conformity with Eq. (9). The mean DC output

$$\sum_0(\lambda_0) = \frac{1}{\pi} \int_{-1}^{+1} \frac{T_0(\gamma) I(\lambda_0 - a\gamma)}{(1 - \gamma^2)^{1/2}} d\gamma$$

The output of odd multiples of the slit oscillation frequency is

$$\sum_{m \text{ odd}}(\lambda_0) = \frac{2}{\pi} (-1)^{\frac{m+1}{2}} \int_{-1}^{+1} \frac{T_m(\gamma) I(\lambda_0 - a\gamma)}{(1 - \gamma^2)^{1/2}} d\gamma \quad (10)$$

and

$$\sum_{m \text{ even}}(\lambda_0) = \frac{2}{\pi} (-1)^{\frac{m}{2}} \int_{-1}^{+1} \frac{T_m(\gamma) I(\lambda_0 - a\gamma)}{(1 - \gamma^2)^{1/2}} d\gamma$$

These signals can be evaluated for any given $I(\lambda)$.

The Chebyshev polynomials are an orthonormal set; so that it is possible to expand any function in a series of Chebyshev polynomials. Thus

$$g(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n T_n(x)$$

where

$$a_n = \frac{2}{\pi} \int_{-1}^{+1} \frac{f(x) T_n(x)}{(1 - x^2)^{1/2}} dx$$

This is just the same integral as appears in Eq. (10) with the function $f(x)$ being $I(\lambda)$ for $\lambda_0 - a < \lambda < \lambda_0 + a$. Therefore the signal outputs of the derivative spectrometer are simply the coefficients of the expansion of $I(\lambda)$ about λ_0 in a series of Chebyshev polynomials:

$$a_m (-1)^c = \sum_m(\lambda_0)$$

where $c = m/2$ for m even, $m/2 + \frac{1}{2}$ for m odd.

Another form in which a_m may be written is given in Ref. 6:

$$a_m = \frac{\int_{-1}^{+1} (1-x^2)^{m-1/2} f^{(m)}(x) dx}{m! \beta_m \int_{-1}^{+1} (1-x^2)^{1/2} dx} \quad (11)$$

Here β_m is the coefficient of x^m in the polynomial $T_m(x)$. This says that the signals of the m -multiple frequency term as detected in the derivative spectrometer are proportional to the m th derivative of the spectral distribution as detected in a conventional spectrometer, taken as a mean over the region $\lambda_0 - a < \lambda < \lambda_0 + a$, weighted by the function $(1-x^2)^{m-1/2}$. The weighting function tends to favor derivatives at points nearer λ_0 ; and the constant of proportionality tends to be smaller as m is greater.

For the second derivative spectrometer,

$$\sum_2(\lambda_0) = - \frac{2a^2}{3\pi} \int_{-a}^{+a} \frac{d^2}{d\lambda^2} \{I(\lambda_0 - \lambda)\} (1 - \{\frac{\lambda}{a}\}^2)^{1/2} d\lambda \quad (12)$$

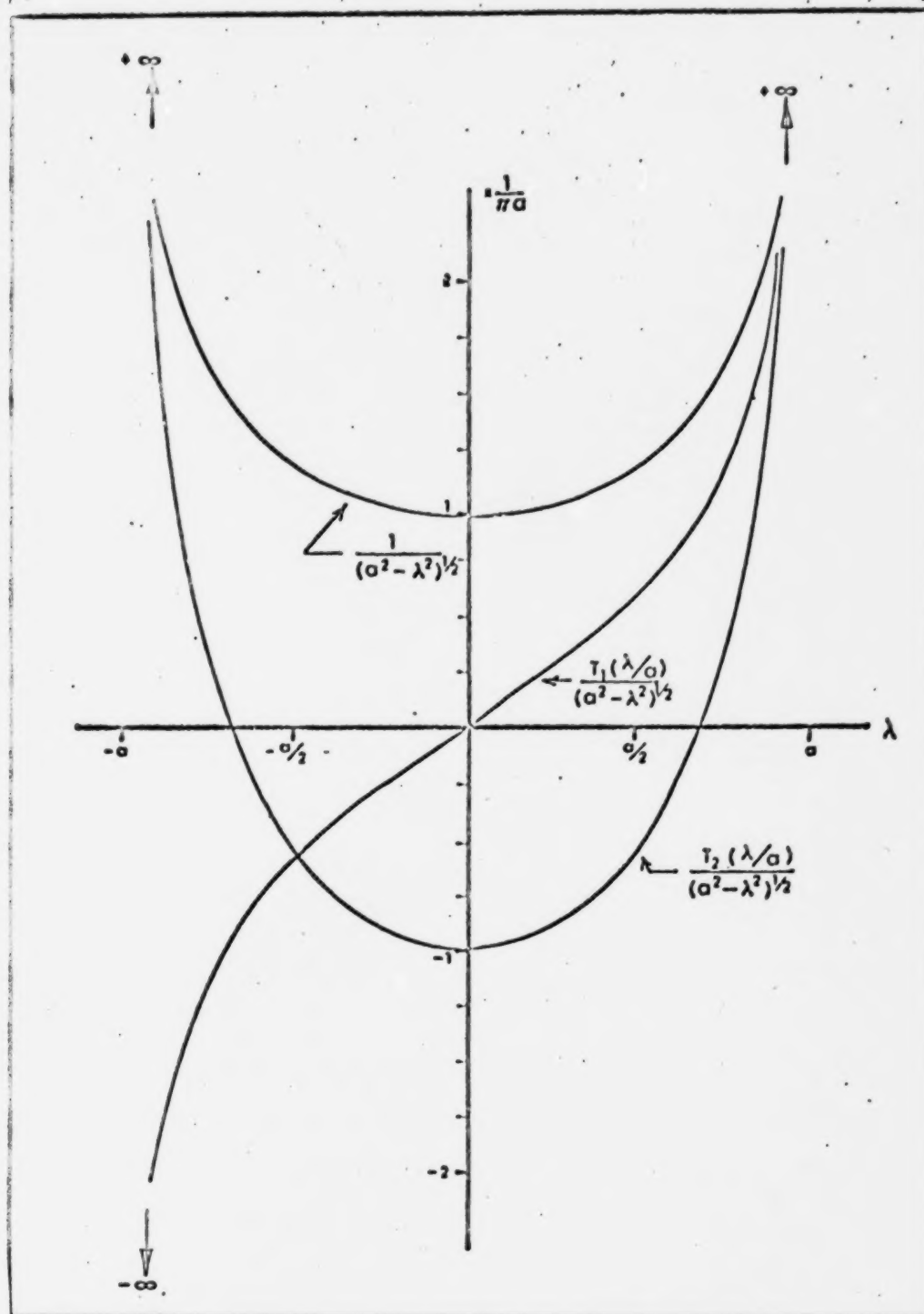


Figure 1. The Functions for $m=0,1,2$ which Are Convolved with the Direct Spectrometer Instrument Function /to Form the M^{th} Derivative Spectrometer Instrument Function

2. DESIGN OF THE d^2 SPECTROMETER

The d^2 spectrometer as presented and analyzed in the previous section is presumed to be built around a conventional spectrometer, modified a) so that radiation leaving the exit slit varies sinusoidally in wavelength with frequency ω about a middle wavelength λ_0 ; and b) so that the portion of the signal varying with twice the frequency 2ω be separately amplified in a tuned amplifier, and thereafter measured.

Wavelength Modulation

The modulation indicated is accomplished by oscillating the entrance slit laterally in a sinusoidal motion. The mechanism which produces this motion is called the "wobbler"; it is described in a master's thesis by W. T. Harris (7). Fig. 2 shows a sketch of the wobbler.

The slit is made by vacuum depositing an aluminium film over the surface of a quartz disc 1 mm thick by 1 in. diameter, while masking the center of the disk with a taut fine wire of the desired width. The disc (a) is then cemented to a carrier plate (b) which is free to oscillate laterally under the constraint of two steel leaf springs (c). A rigid rod connects the carrier with a permanent cylindrical magnet (d), the ends of which move laterally within the hollow cores of two solenoids, one being designated the pickup coil and the other the driver coil. The voltage induced in the pickup coil due to the moving magnet is amplified through a two-stage non-linear transistorized amplifier. Constant non-linearity is provided by a current-dependent supply voltage circuit, and a controllable non-linearity is obtained, using a variable bias resistance to ground for the output stage. The output voltage is fed into the driver

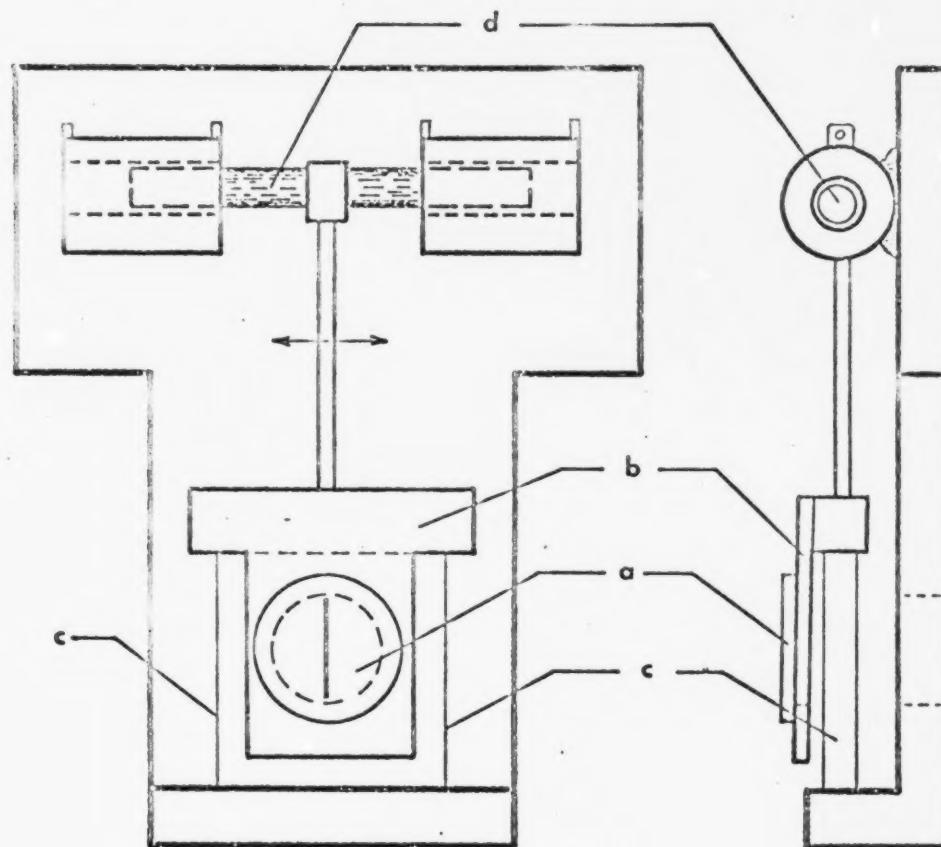


Figure 2. Diagram of the Wobbler

coil of the wobbler.

The wobbler oscillates at the resonant frequency of the spring-mass system. The amplified pickup coil voltage provides a source of energy which is fed through the driver coil to just balance the energy loss due to mechanical and electrical damping at a given amplitude. The variable bias resistor allows the maximum electrical energy output, and hence the wobbler amplitude, to be controllable. The non-linear supply voltage to the amplifier enhances stability in the system over a broad range of amplitude.

The amplitude of the wobbler is measured and displayed on the d^2 instrument panel by use of the pickup voltage, found to vary linearly with the amplitude. Normal applications of the d^2 spectrometer have been made by use of a wobbler amplitude of about .5 mm, and the stability has been confirmed to be within 1 percent over the range 0.3 to 0.8 mm. The amplitude does turn out to depend on the coupling for vibration between the spectrometer and its support; an improved wobbler drive with more energy available is clearly indicated.

The pickup coil voltage is amplified through a separate linear circuit to provide a reference signal used to lock onto the frequency and phase of the modulated intensity signal. The circuitry involved both in the production of a reference signal, and for the amplitude display are shown in Appendix A; they are contained on one 4"x6" printed circuit card.

The d^2 Instrument Electronics

The electronic circuitry in the d^2 electronics package has two functions: a) it provides a DC output voltage proportional to the amplitude of

the $\cos(2\omega t)$ waveform (the $\sum_2(\lambda_0)$ term of the previous section) within the incoming signal; the second purpose b) is to provide an output DC proportional to the constant amplitude ($\sum_0(\lambda_0)$) term in the same input. The ratio of these two voltages constitutes the observable of the d^2 instrument. This ratio is independent of the intensity of the light source, which makes possible on that account the use of substantially higher gains in the generation of signal (a) than would otherwise be possible.

General description

Figure 3 contains a block diagram of the elements which compose the d^2 instrument and representations of voltage waveforms within each element. The detector signal is amplified first by an AC-DC amplifier, the DC output of which is proportional to the $\sum_0(\lambda_0)$ term. The AC portion proceeds to an AC amplifier that has a tuned response peaked at the frequency 2ω .

The amplified AC voltage enters the chopping circuit which blocks or passes the voltage as controlled by the square wave reference voltage. The pulse train begins as the amplified pickup coil voltage of frequency ω . The phase is shifted 90° , the frequency doubled to 2ω and the voltage shaped to that of a square wave pulse train. The selective properties of the chopper can be visualized through Fig. 4.

Line A represents the 2ω chopping frequency and phase. A pulse is allowed through during the shaded times, and is otherwise blocked. Line B is a $\cos(2\omega t)$ waveform, and as indicated, the positive half of the waveform is allowed through. The dotted line represents the integrated voltage. Line C represents a $\sin(2\omega t)$ waveform, and the integrated voltage is zero. Since the function $A \cos(2\omega t - \alpha)$ can be represented

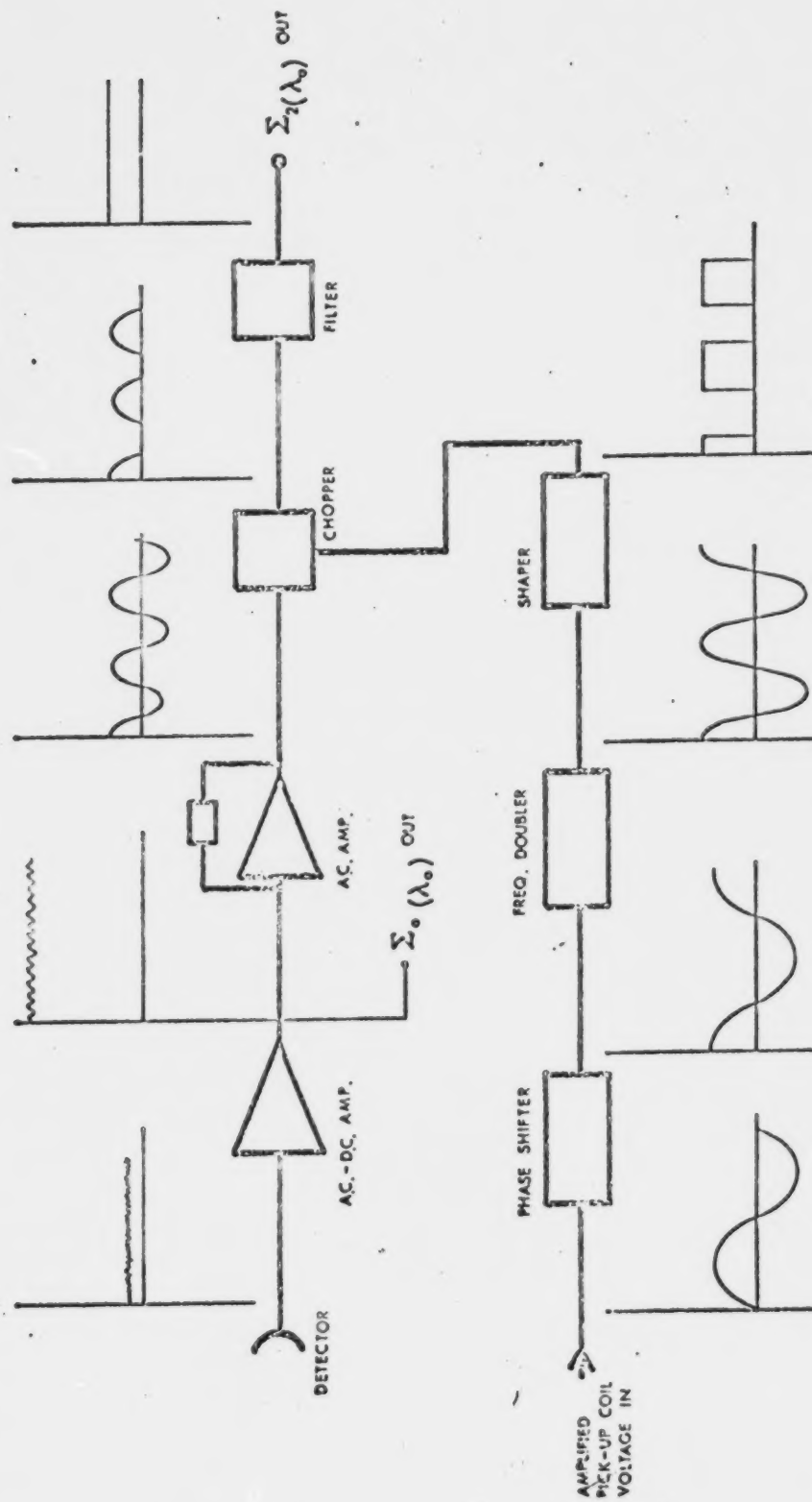


Figure 3. Flow Diagram of the D² Instrument Circuitry

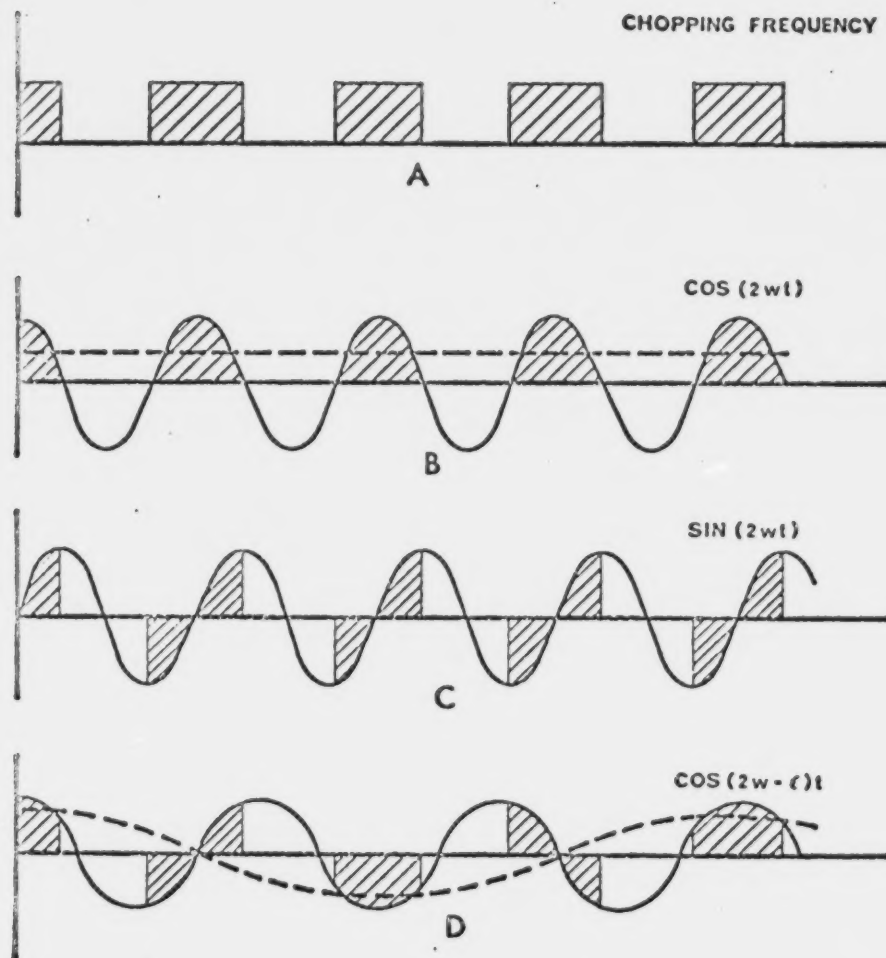


Figure 4. An Illustration of Signal Chopping at Frequency 2ω on $\sin (2\omega t)$, $\cos (2\omega t)$ and $\cos (2\omega - \epsilon)t$

as the sum $B \cos(2\omega t) - C \sin(2\omega t)$, the chopper acts as a phase detector giving a DC voltage proportional to the amplitude B only. Line ϕ is a cosine waveform of slightly different frequency than 2ω . The integrated voltage varies sinusoidally with time as shown, the variation frequency increasing as the frequency difference from 2ω increases. This time-varying voltage can be filtered out by use of a low frequency band-pass filter, the last element shown in Fig. 3. The lower the frequency cut-off of this filter, the narrower the frequency selectivity of the instrument to the $\cos(2\omega t)$ waveform. The output of the filter is the integrated chopped voltage, proportional as was said to $\sum_2(\lambda_0)$.

The AC-DC Amplifier

The AC-DC amplifier is designed around a Fairchild $\mu 4702$ integrated circuit operational amplifier. The detailed circuitry is given in Appendix A. Negative feedback is imposed across the operational amplifier to reduce and stabilize the open-loop gain of 3600 to 500. The amplifier converts the photomultiplier tube output from a current source to a voltage source by grounding the collector current of the tube through a shunt resistor at the input of the amplifier. The input voltage is then the current times the shunt resistance, and the feedback gain $G_{fb} = V_{out}/V_{in}$ reduces to the standard form $G_{fb} = -R_f/R_s$ where R_f and R_s are values of the feedback and shunt resistors, respectively. This formula holds as long as the open loop gain is greater than one, and the input impedance of the operational amplifier (which is 40 K ohms for this case) is much greater than R_s . In terms of photomultiplier current, the amplifier has a linear output of approximately one volt per microamp input current.

The amplifier has an offset current of about $0.4 \mu a$, that is, a

current flow through the shunt resistance when no light is being detected by the photomultiplier tube. Suppression of the offset current and photomultiplier dark current is accomplished by putting two $1\frac{1}{2}$ -volt mercury cells in a high resistance bridge network from which zero to one μ a of DC current can be directed into or out of the amplifier, giving a zero-adjust voltage range of -1 to +1 volts.

The AC-DC amplifier has a linear response over the output voltage range of -4 to +8 volts, above which saturation occurs. A capacitive lag network is employed on the integrated circuit to provide an output voltage roll-off for frequencies above 500 hertz. The output of the amplifier goes to ground through a 50 K ohm resistor, and also is capacitor-coupled to the AC tuned amplifier. The DC voltage drop across the 50K-ohm resistor is proportional to $\Sigma_o(\lambda_o)$.

The Tuned AC Amplifier

The input to the AC amplifier is routed through one of six voltage divider networks selected by the attenuation switch, giving possible attenuations of 1.0, 0.3, 0.11, 0.03, 0.01, or 0.003. The AC amplifier is basically two Fairchild μ A702 amplifiers connected in cascade. The open-loop gain is 140 db which is reduced selectively in frequency by a twin-tee network as a negative feedback element. This network consists of three resistors and three capacitors so selected and coupled that the frequency response of the gain is that of a notch filter, the notch occurring at a selected frequency f_o . As a negative feedback element, the twin-tee provides large negative feedback at frequencies on either side of f_o , and minimum feedback (or maximum gain) at f_o . A gain-limiting feedback

resistor is used in parallel with the twin-tee network to eliminate amplifier instability and quickly dampen "ringing" which occurs at the center frequency due to noise spikes.

The maximum gain of the amplifier is 1000 at a frequency of 88 hertz, the gain being 3 db down at 88 ± 4.4 hertz, giving a circuit Q of 10. The maximum output voltage swing of the amplifier is 15 volts peak-to-peak, above which saturation occurs. An overload light circuit is provided which flashes a neon light whenever the positive output of the amplifier exceeds 7 volts. This circuit consists of a zener diode between the amplifier output and the gate of an SCR to provide a voltage-controlled unlatching switch for the 110vac neon lamp.

As with the AC-DC amplifier, the AC amplifier is also lag-compensated to produce roll-off beginning at 500 hertz. All inputs to the integrated circuits are diode-protected to ground out any destructive high-voltage spikes.

The output of the AC amplifier proceeds through a current-limiting resistor and coupling capacitor to the drain of a p-channel field-effect transistor (FET). The source of the FET is grounded and the drain-to-source resistance is very low (typically 20 ohms) when the gate voltage is zero, but rapidly increases to more than one megohm when the gate voltage exceeds 6 volts. Therefore, the output of the AC amplifier is shunted to ground whenever the gate voltage is zero, and it is therefore chopped in accordance with the reference voltage applied to the FET gate.

The Reference-Signal Conditioning Circuit

The reference signal conditioning circuit transforms the shape, frequency, and phase of the amplified wobbler pickup coil voltage into the

square wave required as the reference voltage on the FET gate. The first element of the circuit is the phase shifter which consists of a PNP transistor connected in a push-pull configuration. A variable resistor and fixed capacitor are connected in series between the transistor emitter and collector so that the voltage drops across the two elements add as phasors to give the voltage across the transistor. Since the voltage drop across the resistor is always 90° out of phase with that across the capacitor, the phase of the voltage at the point between the elements varies with the input voltage phase over a range of 0 to 90° as the resistance of the resistor is changed from large to small values.

The phase-shifting circuit cannot deliver high current, and therefore a high input-impedance amplifier with nearly unit voltage gain, but high current gain is required as the next element in the conditioning circuit. This amplifier consists of two PNP transistors in cascade connected in a common collector configuration. Positive feedback in the form of bootstrapping is used to raise the input impedance to 700Kohms.

The impedance-matching amplifier is followed by the frequency doubling circuit. Three transistors are connected in such a manner that when the output of the initial transistor goes positive, one of the remaining two conducts, and when the output goes negative, the other conducts. A positive voltage is at the common output of the second and third transistors whenever either conducts, so that a signal then results which is twice the frequency of that on the base of the initial transistor.

The frequency-doubled voltage proceeds to an amplifier in the form of a Fairchild $\mu A702$ integrated circuit with negative feedback, where it is amplified to one volt peak-to-peak, and filtered to a nearly sinusoidal

shape. The gain of this amplifier is variable, using a trim potentiometer in the feedback loop.

The output of the amplifier goes directly to the base of another PNP transistor, biased so that the one volt drives the transistor alternately from saturation to cut-off. The transistor output is a 9-volt peak-to-peak square wave. The symmetry of the square wave is set by adjusting the gain of the integrated circuit amplifier. Final biasing of the output produces the required 0 to 9-volt square wave which is applied to the gate of the FET.

The Low-pass Filter and Signal Display Circuits

The chopped amplified ac voltage is applied to the input of a low pass filter which consists of a series resistor R, and a shunt capacitor C, to ground. The output of the filter is the point between the resistor and capacitor and the voltage V_o at this point is given by

$$V_o = \frac{V_{in} [1 - iRC\omega]}{R^2C^2\omega^2 + 1}$$

the magnitude being

$$|V_o| = \frac{V_{in}}{[\omega^2 R^2 C^2 + 1]}^{1/2} \quad (13)$$

The circuit is designed to enable several capacitors to be switched into the C position, giving RC time constants of 0.1, 0.3, 1.0, 3.0, or 10 seconds. For $RC = 1$ second, the filter attenuates the input voltage by a factor of 2 or more when $\omega = 3$ rad/sec or more. Thus, the pass-band for less than 3 db attenuation is 0 to 0.27 hertz. If the RC time constant is increased to 3 seconds, the band pass is reduced to .09 hertz, and for

$RC = 10$ seconds, the band pass is .03 hertz.

Equation (13) is valid only when there is no output current flow from the filter. As output current increases, the output voltage decreases for all frequencies. For this reason, the output voltage is observed by use of a potentiometric recorder. Such a device incorporates a bridge-balancing technique, and so has nearly infinite input impedance at null. This instrument also offers the opportunity to easily divide the filter output voltage by the dc output of the AC-DC amplifier. This latter voltage is used in place of the standard reference voltage within the recorder, which results in a recorder pen displacement proportional to V_o/V_{dc} . This signal is independent of light source intensity variations, since both V_o and V_{dc} are proportional to the intensity of the radiation source. The recorder is further modified so that the zero voltage used to suppress or elevate the input voltage is taken from V_{dc} and so is also proportional to the source intensity. This allows the convenience of setting a desired baseline for the recorder pen and still maintaining a pen displacement independent of the source intensity.

Instrument Limitations

As stated at the beginning of this part of the report, the design criteria for the d^2 instrument were a) a method of sinusoidal wavelength modulation, and b) a method of extracting and measuring the amplitude of the $\cos(2\omega t)$ waveform.

The wobbler, as designed, meets the first requirement, providing a constant frequency sinusoidal modulation with a constant amplitude within ± 1 percent. The electronic circuitry meets the second requirement within

limits to be discussed. The manner in which the electronic elements extract and measure the $\cos(2\omega t)$ waveform was presented graphically. The following analysis defines the limitations.

Consider the time-varying amplified ac signal $V(t)$. Since the amplification is frequency-selective, only components of frequencies near 2ω are highly amplified. The electronic chopping of $V(t)$ by the field-effect transistor is mathematically equivalent to multiplying $V(t)$ by a square wave, $G(t)$, of amplitude either zero or one, of frequency 2ω and with a phase such that $G(t) = 1$ for $-\pi/2\omega \leq t \leq \pi/2\omega$. Such a function can be represented by the Fourier series

$$G(t) = \frac{1}{2} + \frac{2}{\pi} \left\{ \sum_{n=1}^{\infty} \frac{\cos 2(2n-1)\omega t}{(2n-1)} \right\}$$

Therefore, the chopped voltage $V_{in}(t)$ into the low pass filter circuit is

$$V_{in}(t) = V(t) \left[\frac{1}{2} + \frac{2}{\pi} \left\{ \cos 2\omega t + \frac{\cos 6\omega t}{3} + \frac{\cos 10\omega t}{5} + \dots \right\} \right]$$

Now let $V(t) = A \cos(pt)$. Then

$$V_{in}(t) = \frac{A \cos pt}{2} + \frac{2A}{\pi} \left\{ \cos pt \cos 2\omega t + \frac{1}{3} \cos pt \cos 6\omega t + \dots \right\} \quad (14)$$

Each product within the brackets can be expressed as a sum and difference frequency relation. Looking at the first product

$$\cos pt \cos 2\omega t = \frac{1}{2} \cos(p+2\omega)t + \frac{1}{2} \cos(p-2\omega)t$$

The frequency that will be within the pass band of the low-pass filter can only be $(p-2\omega)$ for p nearly equal to 2ω . Specifically, for RC equal to 1 second, the pass band is 0.3 hertz, and $p = 2\omega - 0.3$ hertz will go through without 3 db attenuation. Of course, for this range of p , the leading term in Eq. 14, and all other terms in the expanded product

will not pass.

When $p = 2\omega$, then

$$\cos^2 2\omega t = \frac{1}{2} (1 + \cos 4\omega t)$$

and there exists a pure dc component, in which case the filter output voltage $V_0 = A/\pi$.

It is true that the filter will give pure dc outputs for input voltages of frequency 6ω , 10ω , 14ω , etc., coming from each of the other product terms in Eq. 14. This is the primary reason for using the tuned amplifier, for all of these frequencies (and also low frequencies which could affect the output through the leading term) are far outside the peak response of the ac amplifier. Note also that the products are naturally attenuated by the $1/(2n-1)$ factor.

If $V(t)$ is set equal to $A \sin(pt)$, the same analysis will show that no pure dc term is ever possible, but the same difference frequency oscillations are present.

In summary, the analysis shows that the dc voltage on the output of the filter is proportional to the amplitude of the $\cos(2\omega t)$ term, other sources of dc being highly attenuated by the nature of the chopping signal and the tuned ac amplifier. Noise, in the form of low frequency oscillations, is restricted by the chopping circuit and the low pass filter, to a band about frequency 2ω . This band can be as narrow as $2\omega \pm 0.03$ hertz, using an RC time constant of 10 seconds. All other frequency noise is rejected either by the amplifier, or filter, or both.

3. THE d^2 SPECTROMETER APPLIED TO THE DETECTION OF AIR POLLUTION

Air pollution is defined as the presence in the air of substances which interfere with man's comfort, safety or health. The gases now considered of primary importance in the category of pollutants include sulfur dioxide, carbon monoxide, nitric oxide, nitrogen dioxide, hydrogen sulfide, ozone, and ammonia. The concentration levels that are judged to be quite definitely harmful, and therefore to require remedial action are in the process of analysis. A series of air quality criteria will be established by law in the course of the next months and years; and procedures will be devised and implemented to make possible control of air quality. Such control will of necessity require monitoring of pollutant concentrations.

The concentration levels of pollutants that constitute inadmissible levels are expected to be low in comparison with those concentrations previously encountered in chemical engineering. Thus the criterion (8) for sulfur oxides is a maximum of 0.11 parts per million (ppm) for 3 to 4 days, or when the annual mean level exceeds 0.04 ppm. Adverse effects on materials occur at an annual mean of 0.12 ppm and on vegetation at an annual mean of 0.03 ppm. Some data on pollutant concentration levels measured in several cities are given in Table 1 (9).

When the need for monitoring air pollutants was first recognized, techniques were adapted from instrumentation used in the chemical industry. Instruments generally measured by use of wet chemistry the compounds formed when polluted gas was bubbled through an appropriate solution. The material formed by interaction with the pollutant was then measured quantitatively by observation of some characteristic physical property.

TABLE I.
URBAN POLLUTION CONCENTRATIONS, 1966

City	Yearly Average, ppm/Max. Daily Average, ppm				
	CO	NO	NO ₂	SO ₂	NH ₃
Chicago	12.5/32.3	0.10/0.36	0.06/0.15	0.08/0.79	
Cincinnati	4.9/16.5	0.04/0.36	0.04/0.10	0.03/0.18	
Denver	7.9/20.3	0.03/0.25	0.03/0.09	0.01/0.06	0.16/0.39
Philadelphia	6.8/25.0	0.06/0.56	0.04/0.14	0.09/0.46	
St. Louis	5.8/16.7	0.03/0.25	0.03/0.12	0.04/0.26	0.07/0.21
Washington	3.3/22.9	0.04/0.41	0.04/0.10	0.04/0.25	

Wet chemistry is at present the primary method of detecting several important pollutants, such as sulfur dioxide by the West-Gaeke method (10), nitric oxide and nitrogen dioxide by the Saltzman reaction (11) and ozone by the oxidation of potassium iodide (12). These methods, and others developed more recently, can be extremely sensitive. They have a common disadvantage in that the methods require suitable chemicals of proper purity and in some cases freshness, and the adjustment of flows often requires a certain amount of attention. Furthermore some of the methods are subject to interference in that other materials than the intended pollutants may produce the same observable.

The problem of interference would be greatly relieved if a physical rather than a chemical property of the pollutant were detected. Efforts are now under way by industry and air pollution control agencies to develop a so-called second generation of instruments with this common characteristic.

The d^2 spectrometer as applied to the detection of air pollutants is a second generation instrument. The physical property that is directly detected is the ultraviolet or visible absorption spectrum characteristic of the molecular gas under study.

The history of the development of the d^2 instrument has been reviewed already. It began as a correlation spectrometer; but at length the mask as used in that technique was discarded in favor of the single slit. A schematic of the present version of the instrument is shown as Fig. 5. A radiation source, either a deuterium arc or an incandescent light, is placed in front of a spectrometer with entrance slit replaced with one mounted on a wobbler; the exit slit is fixed. The monochromatic radiation emerging from the spectrometer traverses the analyzing cell with pathlength L , containing a pollutant at concentration c , and is received at the detector. The d^2 instrument as described above, provides a signal proportional to a weighted mean of the second derivative with respect to wavelength of the spectral intensity convolved or smeared by the spectrometer slit function. The recorder then displays the ratio of the derivative signal to the signal proportional to the average dc intensity.

The observable.

If $I_0(\lambda)$ is the spectral intensity of the source, then with gas at concentration c , in a cell of path length L , the spectral intensity that reaches the detector is

$$I(\lambda) = \int_{-\infty}^{+\infty} I_0(\lambda') e^{-k(\lambda')cL} S(\lambda-\lambda') d\lambda'$$

If $k(\lambda')cL$ is much less than one,

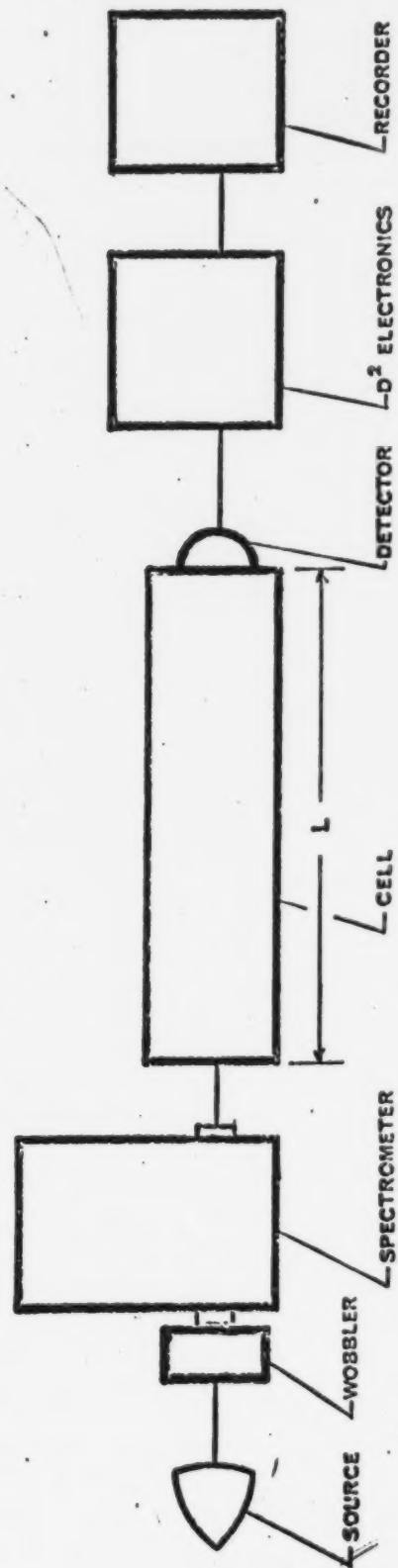


Figure 5. Block Diagram of the D² Air Pollution Detection System

$$\begin{aligned}
 I(\lambda) &= \int_{-\infty}^{+\infty} I_0(\lambda') (1 - k(\lambda') cL) S(\lambda - \lambda') d\lambda' \\
 &= \int_{-\infty}^{+\infty} I_0(\lambda') S(\lambda - \lambda') d\lambda' - cL \int_{-\infty}^{+\infty} k(\lambda') I_0(\lambda') S(\lambda - \lambda') d\lambda'
 \end{aligned}$$

In both integrals $I_0(\lambda')$ is a function slowly varying with wavelength, which remains essentially constant over any interval $(\lambda - \lambda')$ in which $S(\lambda - \lambda')$ is non-zero (recall that $S(\lambda - \lambda')$ is nearly a triangular function with the base equal to twice the spectrometer spectral slit width). Therefore the integrals reduce to

$$\begin{aligned}
 I(\lambda) &= I_0(\lambda) - I(\lambda) cL \int_{-\infty}^{+\infty} k(\lambda') S(\lambda - \lambda') d\lambda' \\
 &= I_0(\lambda) \{ 1 - k'(\lambda) cL \}
 \end{aligned} \tag{15}$$

where $k'(\lambda) \equiv \int_{-\infty}^{+\infty} k(\lambda') S(\lambda - \lambda') d\lambda'$ is the new smeared or low-resolution absorption coefficient.

It should be noted that the exact form of the absorption coefficient for molecules is rarely known and never used. It would describe exactly each rotational line that comprises a band. What is used instead is a measured value $k'(\lambda)$ which is always distorted by whatever instrument was used in the best observations made; alternatively, a model may be developed to predict the profile of a band without describing the individual lines precisely. The important point is that $k'(\lambda)$ in Eq. 15 is a unique function determined by the absorbing molecule and a specific spectrometer slit function.

The second derivative of Eq. 15 is

$$\frac{d^2 I(\lambda)}{d\lambda^2} = \frac{d^2 I_0}{d\lambda^2} - \frac{2dk}{d\lambda} \frac{dI_0}{d\lambda} cL - \frac{d^2 k}{d\lambda^2} cL I_0(\lambda)$$

As previously stated, the ratio from the d^2 instrument $\Sigma_2(\lambda_0)/\Sigma_0(\lambda_0)$ is proportional to the weighted second derivative of $I(\lambda)$ with respect to λ over an interval about λ_0 , divided by the mean intensity at λ_0 .

As these weighted means approach the actual values, the ratio signal

$$\begin{aligned} S_R &\rightarrow \frac{d^2 I(\lambda_0)}{d\lambda_0^2} / I(\lambda_0) \\ &= \frac{1}{I_0} \frac{d^2 I_0}{d\lambda^2} - \frac{2dk}{d\lambda} \frac{dI_0}{d\lambda} \frac{cL}{I_0} - \frac{d^2 k}{d\lambda^2} cL \quad (16) \end{aligned}$$

Each term is now independent of the source intensity. When the center wavelength λ_0 is slowly varied over any region within which the source has some intensity, the record of S_R traces out the so-called derivative spectrum of the particular absorbing gas under study. Figures 6 and 7 are spectra for six pollutants of major importance.

The pattern of the spectrum identifies the gas, and any peak can be used to measure the concentration. The vertical distance between the peak of the curve and the mean of the two adjoining minima is the observable. For this observable, because the first derivative of the intensity I_0 is presumed nearly constant, the observable is a measure of the curvature at the bottom of the absorption band, where the first derivative of the spectrum is zero. It is found, as anticipated, to be proportional to cL .

The particular peak selected for measurement of each gas is chosen so as not to interfere with other spectra. In case interference does occur, it is readily observed by the distortion which is produced in the

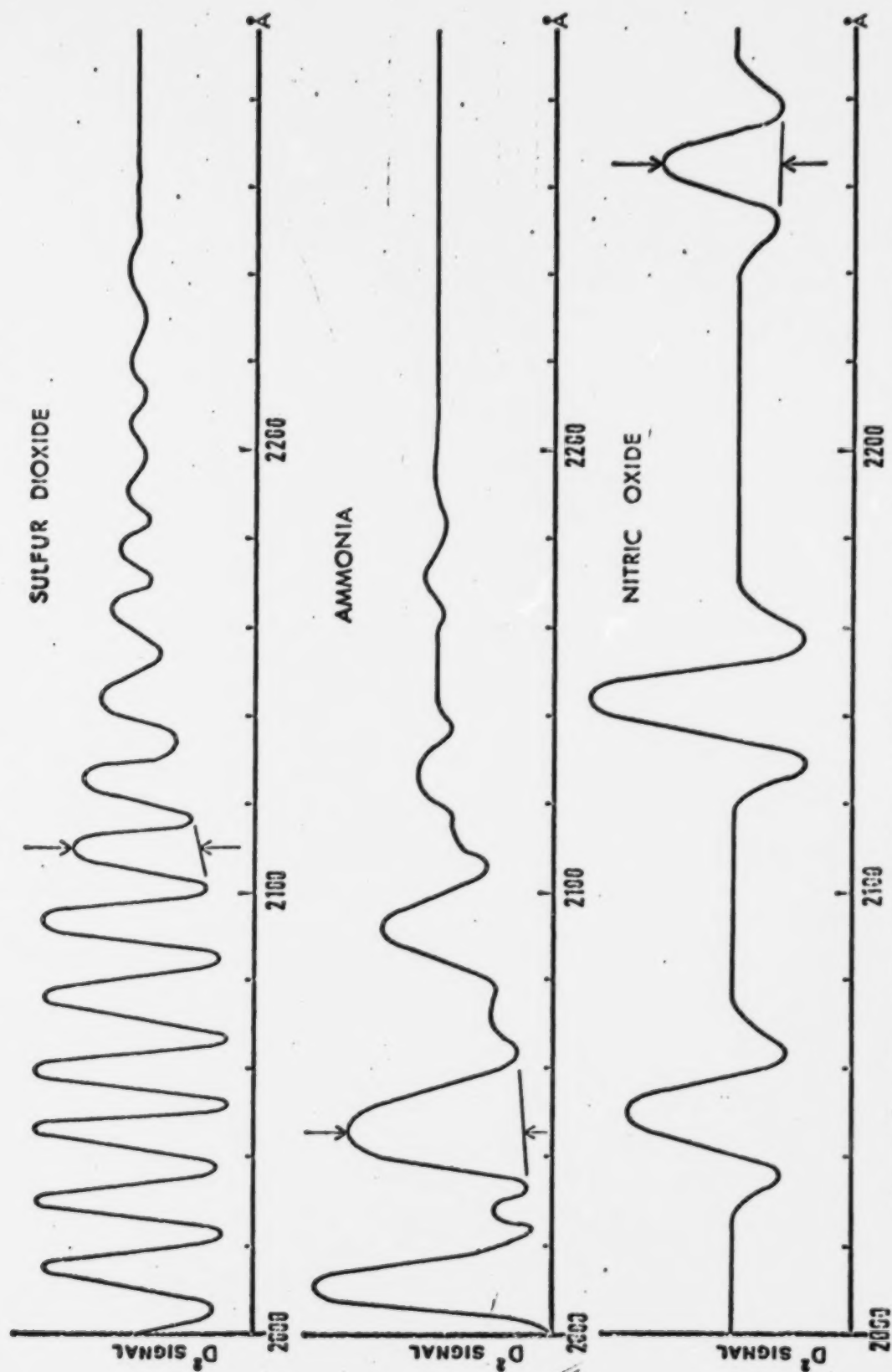


Figure 6.. Second Derivative Spectra of Sulfur Dioxide, Ammonia and Nitric Oxide

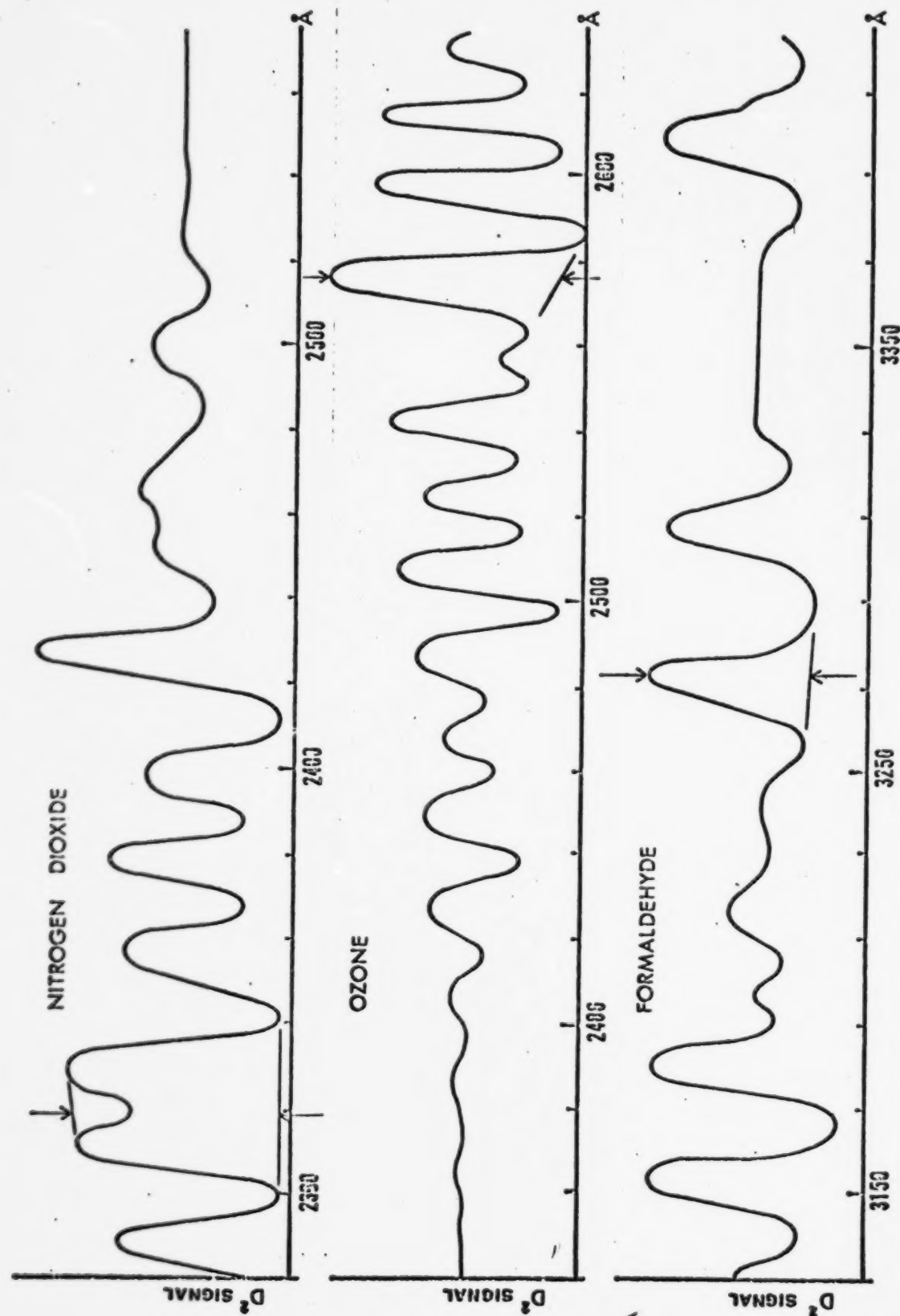


Figure 7. Second Derivative Spectra of Nitrogen Dioxide, Ozone and Formaldehyde

peak shape. If two or more peaks do interfere, it is possible to extract information concerning the interfering gases. In essence, the signals obtained in the d^2 instrument are linear with the concentrations c_1 of whatever gases are present; therefore the curvatures, insofar as they are directly superposed, are additive, and can be disentangled by subtraction.

Detailed Description

The present form of the system used for air pollution studies is shown in Fig. 8. The tee-shaped package is 48 inches wide and 30 inches long, and contains the radiation source and power supply, the spectrometer, and the analyzing cell. The radiation source is a deuterium arc lamp, model D102, manufactured by Quartzlampen GmbH of West Germany, mounted in a specially designed housing which permits lateral and vertical adjustment of the lamp. The lamp is powered by a circuit, housed in the chassis at the end of the base, which full-wave rectifies and filters 110 vac to give the required dc voltage. The lamp has to be started by use of a tesla coil. A ballast resistor is used in series with the arc--a 110vac light bulb has ideal characteristics for this purpose: the power of the lamp can be set by the wattage of the ballast bulb. A quartz collector lens in the lamp housing directs radiation through the 100 micron slit of the wobbler, mounted on the entrance port of the spectrometer.

The spectrometer is a small Jarrel-Ash quarter-meter grating instrument, model 82-405, marketed under the name "Minichromater." It contains a 20 mm x 30 mm reflecting grating with 1180 grooves per mm, which produces a reciprocal spatial dispersion of 33 Å per mm at 2500 Å.

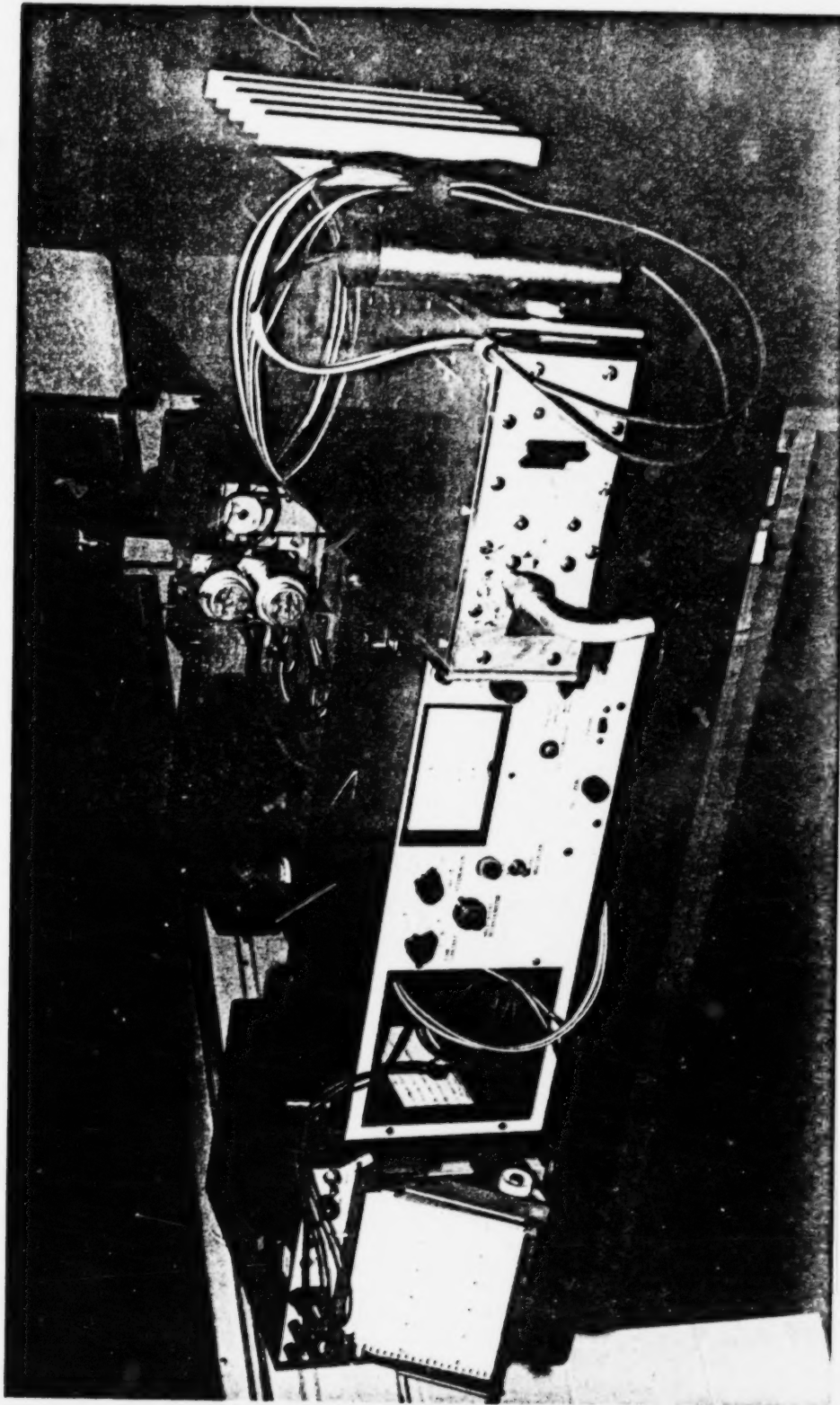


Figure 3. Photograph of the D² Air Pollution Detection System

The dispersed radiation leaves the spectrometer through the stationary 100 micron exit slit and proceeds through a short interconnecting tunnel to the gas analyzing cell, termed the HEW cell. It is through this cell that air to be analyzed for pollution content is drawn by a small 7-watt fan at a volume rate of about 10 liters/min. Figure 9 is a diagram of the optical system within the HEW cell. A small plane mirror, M_1 , directs radiation to the collecting mirror M_2 which is parabolic with an 18-inch focal length. A collimated beam then travels back and forth between plane mirrors M_3 and M_4 , so aligned as to be parallel in the vertical plane, but slightly askew in the horizontal plane. The skew angle is adjustable and is set so that the radiation beam walks across the cell and back to the focusing mirror M_5 , while traversing the length of the cell either 3, 5, 7, or 9 times, depending on the setting of the mirror M_3 . For general operations, the plane mirrors are set for 7 passes of the cell, giving a total radiation pathlength within the cell of 8.72 meters. The parabolic focusing mirror then directs a converging beam into the window of an RCA-7200 photomultiplier tube.

The tube contains 10 dynode stages, requiring a total operating voltage of -1000 vdc, which is supplied by two 510-volt dry cell batteries contained within the d^2 instrument case. A shielded cable conducts the operating voltage to the tube and the tube anode current to the d^2 instrument. The two voltage outputs of the d^2 instrument are ratioed and displayed on a modified Minneapolis Honeywell potentiometric recorder.

Two major problems were encountered and solved during the development of the HEW cell. First, factory-coated mirrors were found to be useless in such a multiple-reflection system. The reflectance of all metals tends to decrease for radiation near the vacuum ultraviolet; but pure aluminum can

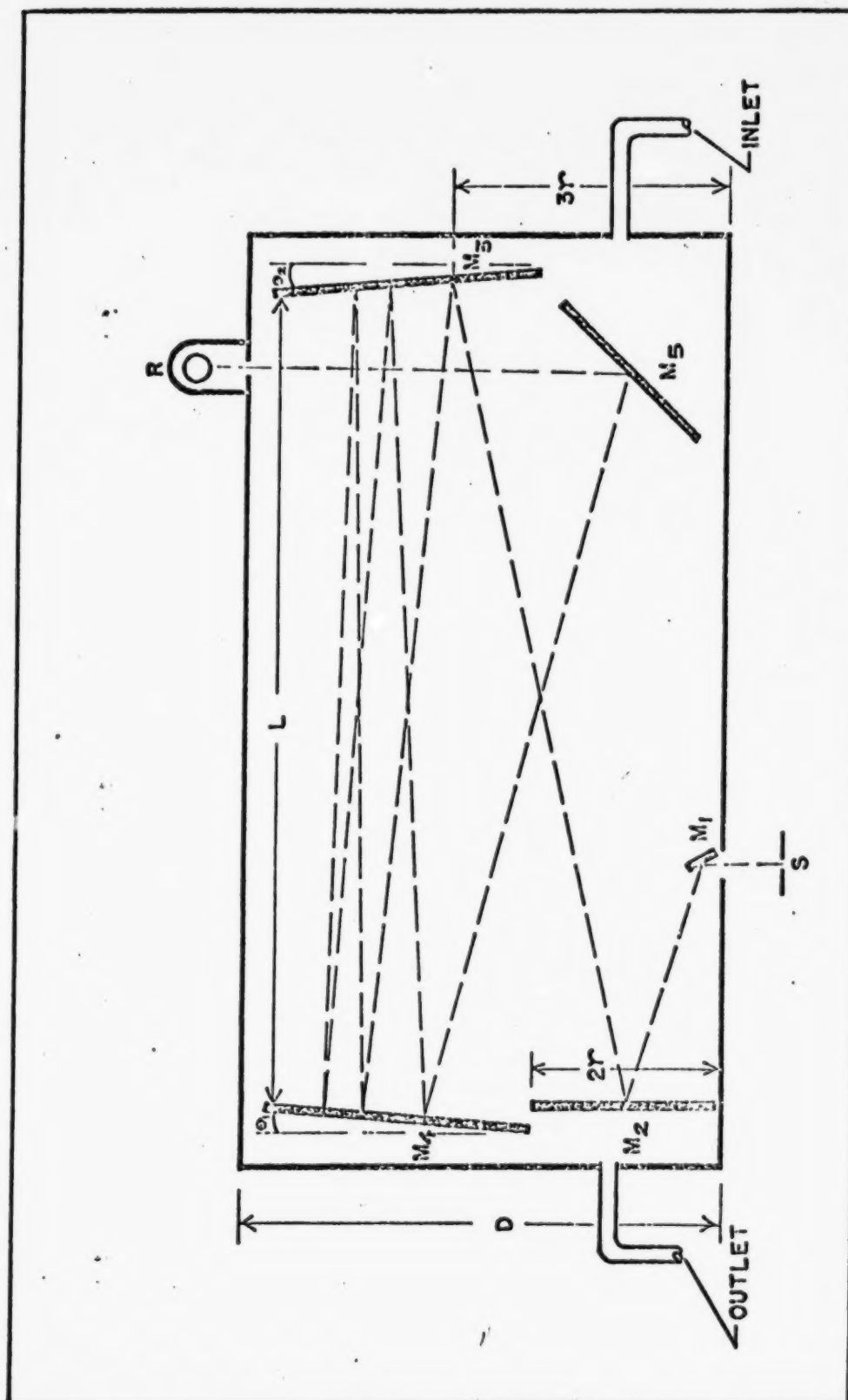


Figure 9. Optical Geometry of the HEW Cell

be vacuum-deposited to give reflectance in excess of 95%, down to 2000 Å. However, overcoats of silicon monoxide used to protect the aluminum begin absorbing extensively below 3000 Å. Special mirrors, designed for use in the ultraviolet, with overcoats of magnesium fluoride were found to be quite inferior to pure, uncoated aluminum. Note that, in the HEW cell set for 7 passes, there are 9 reflections so that the fraction of the incoming intensity lost due to absorption at the mirrors is equal to $1-(R)^9$ where R is the reflectance at a particular wavelength. If $R = 0.9$, the loss is 61 percent; if $R = 0.8$, the loss is 87 percent. In our present procedure, all mirrors used in multiple-reflection systems are stripped of their original coating and carefully recoated with pure aluminum, using a rapid vacuum-evaporation technique.

The second problem encountered was difficulty in maintaining optical alignment within the HEW cell after transport of the system to and within a station wagon used for field tests. Because of the long folded radiation path, small deflections of the cell structure resulted in major misalignments within the optical system. This problem was eliminated by use of a double wall construction to form the cell, sandwiching a polystyrene foam core between aluminum skins and then firmly mounting the cell to a rigid closed box base to insure rigidity between the spectrometer and the cell optics. The result was a system insensitive to shocks and vibration encountered during operational portage.

Operation

During operation of the d^2 air-pollution detection system, intervals of wavelengths which contain a particular absorption band of a particular pollutant are slowly scanned. The derivative spectra of these specific

molecular bands are then recorded, and the peak heights, as previously discussed, are multiplied by calibration factors to give the concentration of the different pollutants within the cell.

Scanning is accomplished by two motors, geared to independently drive the spectrometer mechanism which varies the grating angle. One motor operates at a slow speed, producing a scan rate of $20 \text{ \AA}^{\circ}$ per minute; the other provides a fast scan rate of $100 \text{ \AA}^{\circ}$ per minute. Both motors are reversible. Scanning over a region containing an absorption band is always accomplished by use of the slower motor, while movement from region to region is done at the fast rate.

An electro-mechanical system was devised to provide operation in either manual or automatic modes. The manual mode simply provides power for either motor in either the forward or reverse direction. The automatic mode provides a means of scanning several preselected regions consecutively and then recycling to repeat the program. This is accomplished by a sequencing belt driven from a sprocket on the wavelength drive shaft. The belt contains two sets of tabs which trip two microswitches; one microswitch activates either the fast or slow motor in the forward direction; the other switch activates the fast motor in either the forward or reverse direction. In the field, a programmed belt is often used that provides automatic multiple data on ozone, nitrogen dioxide, nitric oxide, sulfur dioxide and ammonia.

System Calibration

The Static Method

Two calibration methods have been used for those gases that are stable

in a pure state, and in air or nitrogen. The method used during the early development stages of the air pollution instrument, termed the static method, consists of mixing a small volume of the pure gas with a large volume of a carrier gas, either air or nitrogen, within a mylar bag. The mixture of known concentration is then passed through a one-centimeter pathlength quartz cell which has been inserted into the radiation path of the air pollution instrument, such as within the tunnel between the spectrometer and HEW cell. Since the peak height is proportional to the concentration times the pathlength, the sensitivity of the instrument for the HEW cell of known pathlength can be determined. This method of calibration allows the concentration of calibrating mixture to be very large; nearly 1000 times the ambient expected levels, since the ratio of pathlengths is nearly 1000:1. Measurement errors during mixture are therefore minimal, since a flow meter is used to measure the volume of the carrier gas, of the order of liters, and a syringe is used to measure the quantity of injected pollutant gas, of the order of milliliters. An accurate mixture in parts per thousand is then prepared which will give a signal equivalent to concentrations within the HEW cell of parts per million.

Precautions must be taken throughout the calibration procedure to insure that the concentration flowing through the calibration cell remains the same as that originally mixed. The pollutant gases readily adsorb onto and absorb into certain solid materials. Mylar is chosen for the bag material for this reason, primarily because the use of mylar bags is at the moment standard in the field. Although mylar presents a relatively inactive surface for these processes to occur, bags must be pretreated by contact with the pollutant gas in low concentrations from 12 to 24 hours prior to a calibration for that gas, particularly when working

at concentrations below one part per 10,000. Also, glass transfer tubing is used from the bag to the cell, with flexible joints of teflon or mylar inner-wrapped plastic tubing. Finally, flow rates through the cell are maintained at a level such that an increase in flow does not produce an increase in signal. This required flow rate varies from gas to gas.

The Dynamic Method.

Since the interaction of pollutants and surfaces was observed to affect noticeably the measured concentration of a calibration mixture in the static method, it was desired to develop a calibration procedure that would utilize the complete system including the HEW cell, so that wall effects within the cell could be evaluated. Such a procedure requires the precise formulation of a gas sample containing the pollutant at a known concentration. The method devised operates by injecting the pure pollutant gas, or the pollutant gas diluted by a relatively small factor, at a known low flow rate into a stream of carrier gas, flowing at a known high flow rate. The mixture then flows through the HEW cell where the pollutant is detected.

The pollutant was injected from a 10 ml glass syringe, mounted in a holder with the needle projecting into a one-half inch diameter polyethylene tube through which the carrier gas flows. The syringe plunger is driven into the body at a slow constant rate by a presser foot whose linear motion is derived from a threaded shaft turned by a 2/5 RPM timing motor. The presser foot moved at a rate of one inch per hour, producing a pollutant volume flow rate into the carrier gas of 0.074 ml per min. The carrier gas flow is regulated to provide the desired concentration. For example, a flow rate of 18.4 liters per minute results in a concentration of 4 ppm. The pollutant within the syringe can be diluted up to one part in 20 to

also regulate the final concentration. The system is designed to hold up to three syringes, thus enabling the formation of a multi-component pollutant sample.

Figures 10 through 14 are calibration data for several pollutants. All data were obtained by use of the dynamic method except that for ozone, which will be discussed separately. It is apparent that a straight line is the best fit for data points at flows above 5 liters per minute, thus supporting the assumptions of the previous analysis. Figures 12 and 13 for nitric oxide and nitrogen dioxide demonstrate the removal of the pollutant through wall effects at low flows, since these data generally fall above the best straight-line fit of high-flow data points, the deviation increasing as the flow rate decreases. Pure nitrogen was used as the carrier gas with these two active gases, in order to eliminate oxidation reactions.

A Calibration Procedure for Ozone

Ozone is extremely active and cannot be contained within a vessel without a reduction in concentration with time, which makes calibration by either the static or dynamic methods impossible. It can be generated by producing an electrical arc discharge in the presence of air, and commercial devices are available for this purpose. The calibration method used to obtain the data points in Fig. 14 is based on the extremely high absorption continuum exhibited by ozone in the region of 2500 Å. The bands which are sensed by the d^2 spectrometer sit atop this continuum.

Unknown quantities of ozone are generated and drawn through the HEW cell. The reduction in the radiation intensity due to the continuum absorption is monitored through the $\sum_o(\lambda_o)$ dc signal at 2570 Å at which

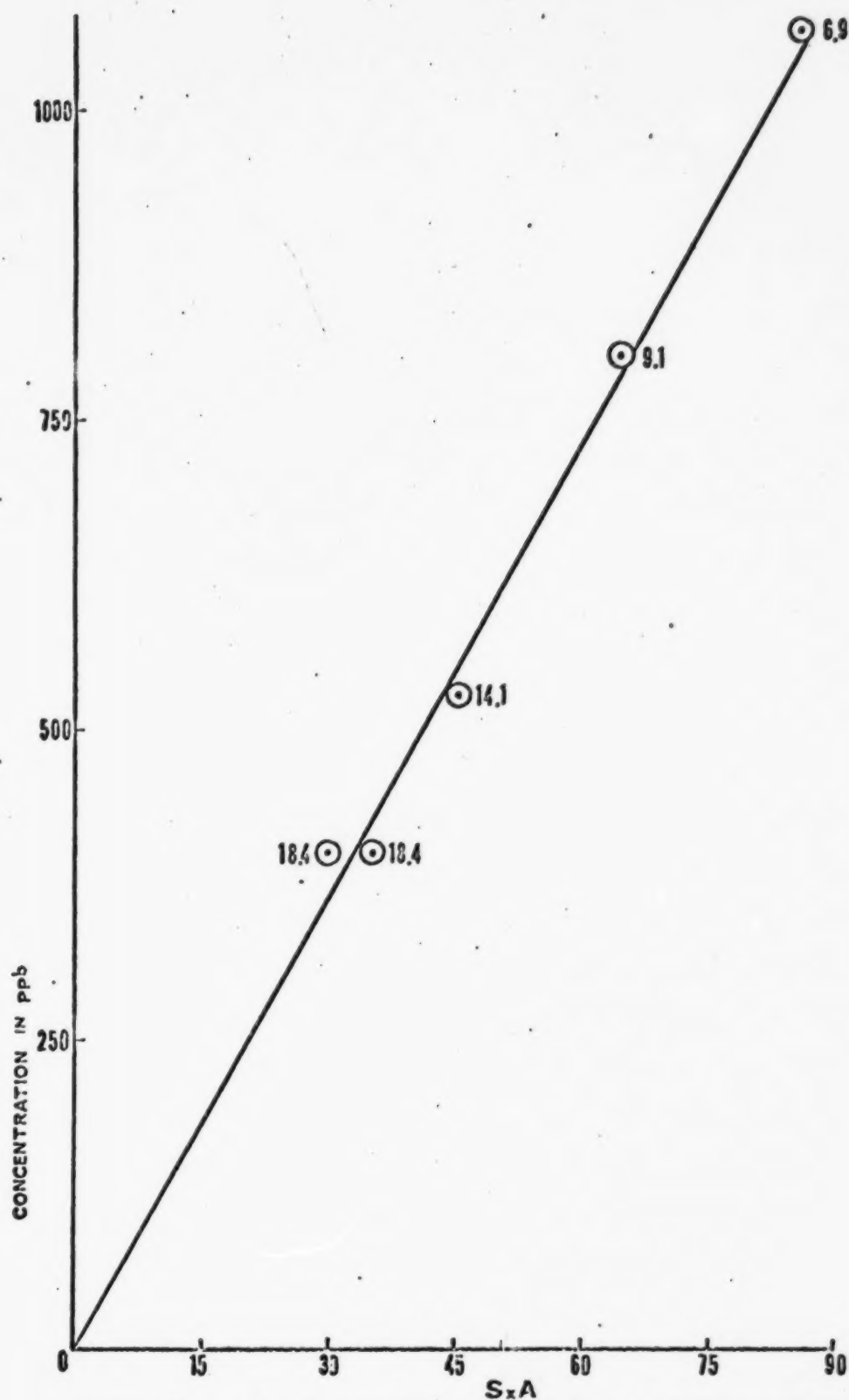


Figure 10. Calibration Data for Ammonia. (Carrier gas flow rate for each datum point is given in liters per minute.)

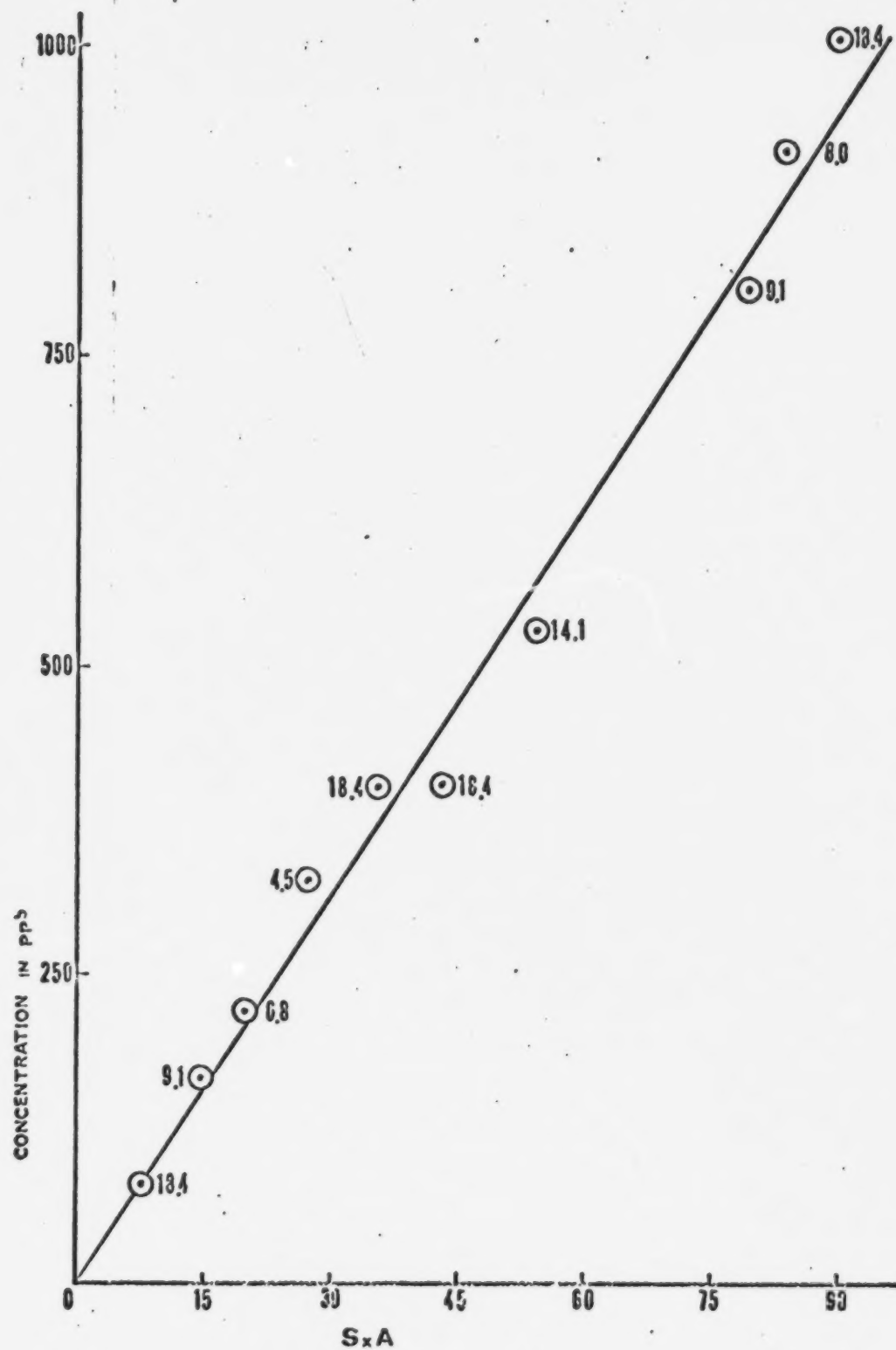


Figure 11. Calibration Data for Sulfur Dioxide. (Carrier gas flow rate for each datum point is given in liters per minute.)

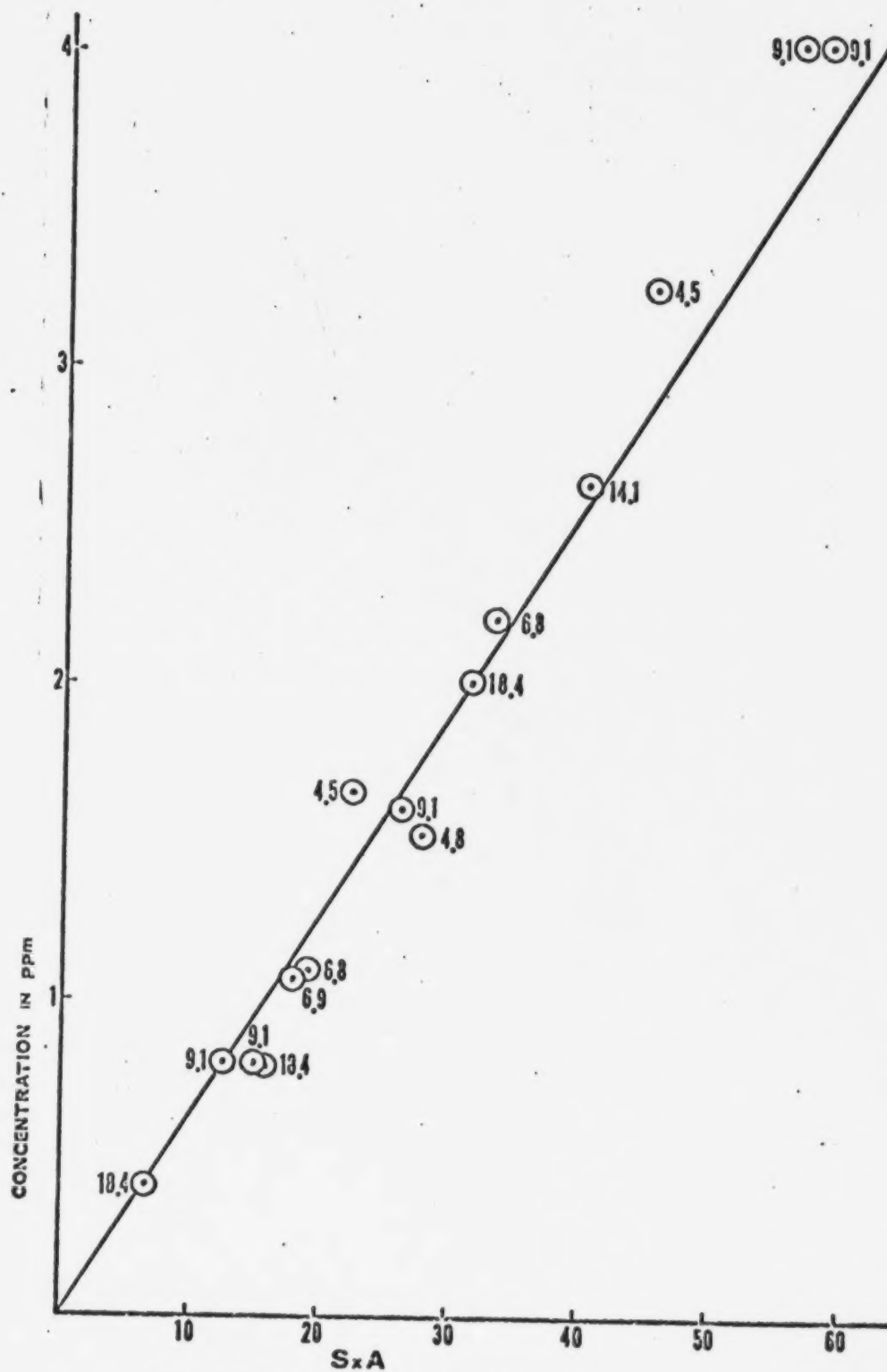


Figure 12. Calibration Data for Nitric Oxide. (Carrier gas flow rate for each datum point is given in liters per minute.)

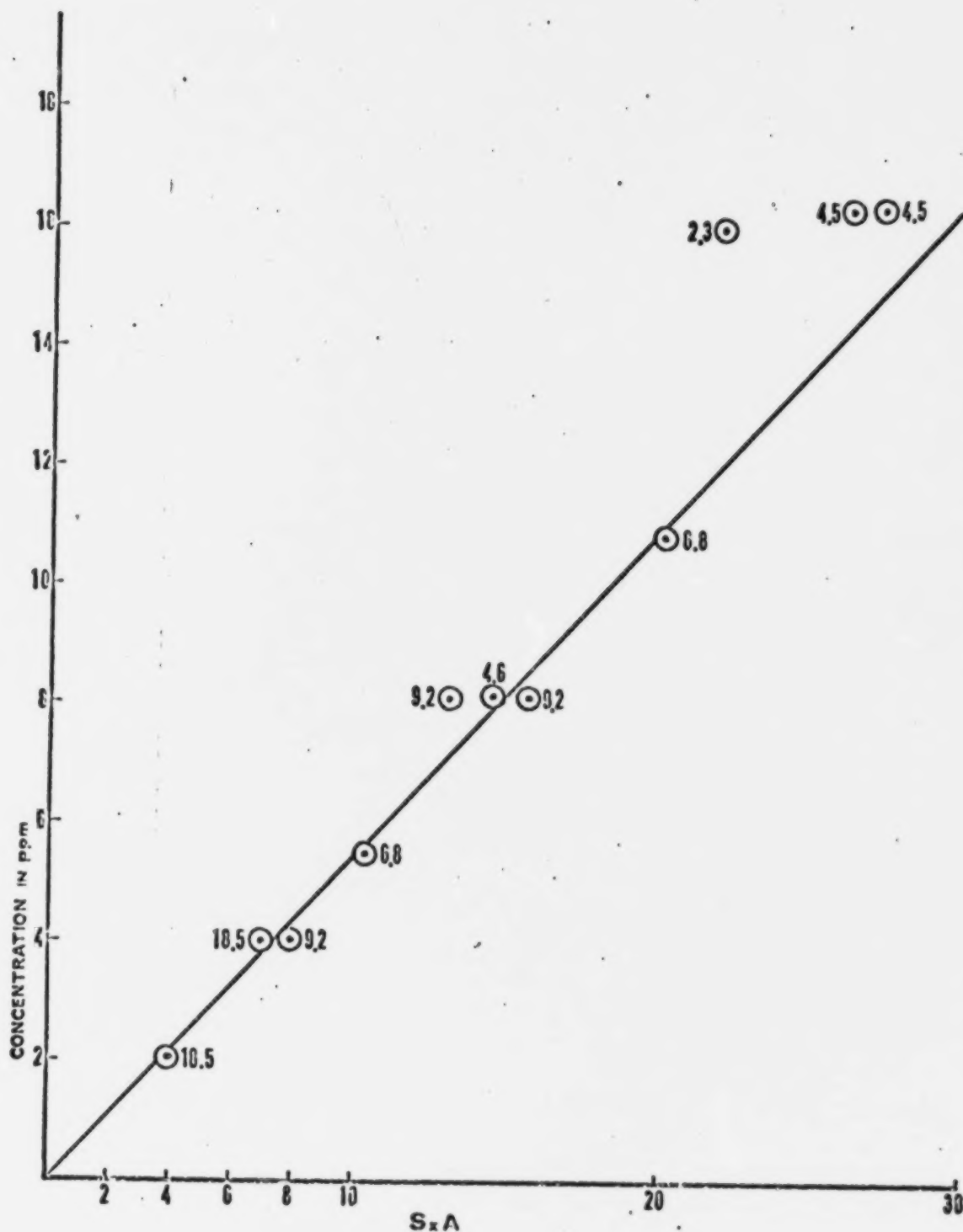


Figure 13. Calibration Data for Nitrogen Dioxide. (Carrier gas flow rate for each datum point is given in liters per minute.)

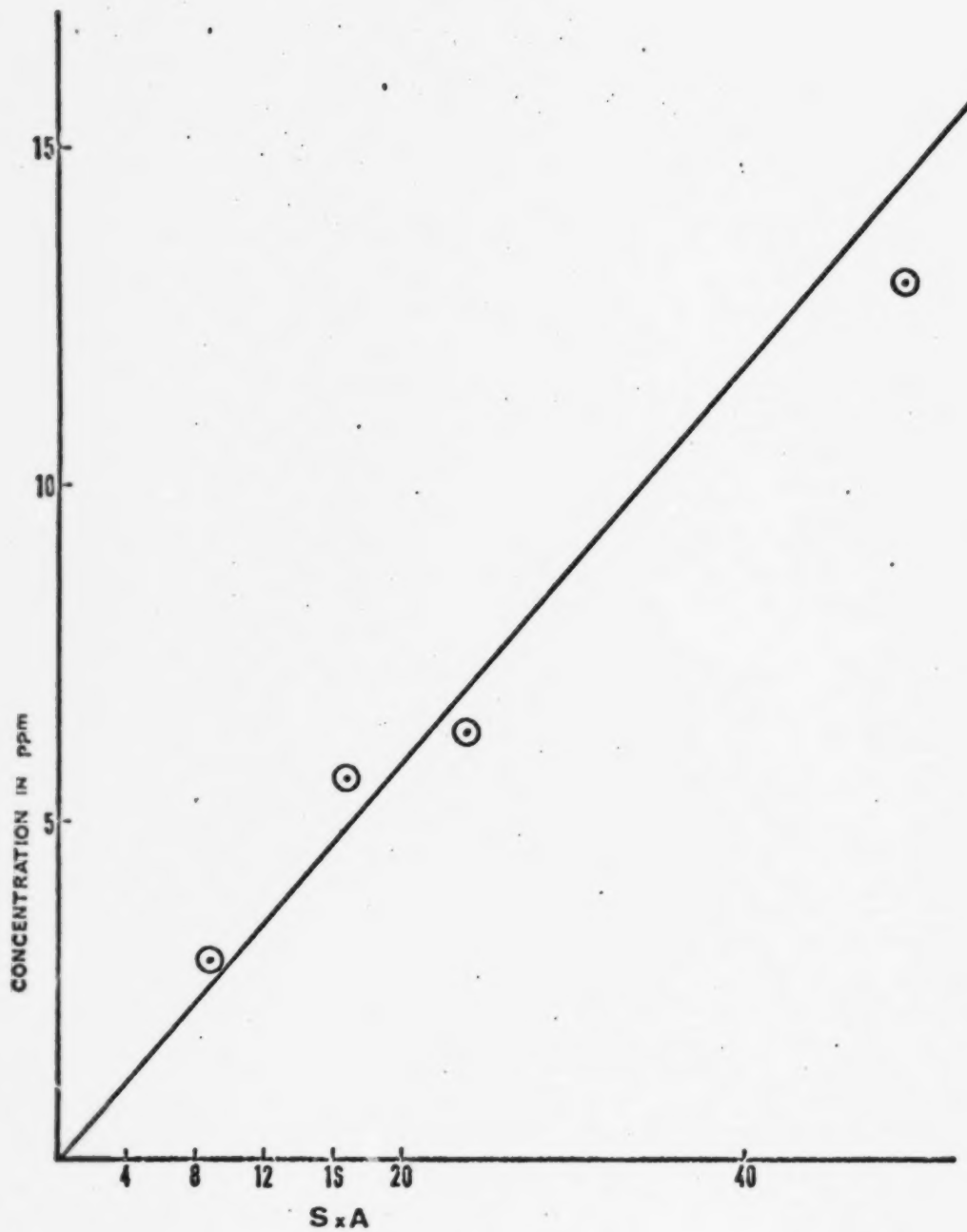


Figure 14. Calibration Data for Ozone

the value of absorption coefficients as given in Ref. 13, as $135 \text{ (atm-cm)}^{-1}$. The bands are then scanned and the peaks recorded. For each concentration, the value $\ln(I_0/I)$ which, by Beer's law, equals kL , is determined and the concentration $c = 1/kL \ln(I_0/I)$ is calculated. A linear derivative observable is possible in certain cases such as this where kL is not small compared to one, because the total absorption coefficient can be represented as the sum of the continuum and band terms. Thus

$$\begin{aligned} I &= I_0 \exp(-kL) = I_0 \exp(-k_c L - k_b L) \\ &= I_0 \exp(-k_c L) \exp(-k_b L) \\ &= I'_0 \exp(-k_b L) \end{aligned}$$

As long as the continuum coefficient k_c does not vary rapidly with wavelength and $k_b L$ is much less than one, linear variation of signal with concentration is maintained. The effect of the continuum absorption is essentially to reduce the dc signal; therefore the output of the d^2 instrument, which is the ratio of the ac and dc signals, is completely unaffected by the continuum absorption, its effect being precisely the same as though there were a reduction in signal due to some other cause.

The difficulty involved in this type of calibration procedure lies in the fact that a measurement of the absolute radiation intensity is required, which is sensitive to fluctuations in the source intensity. However, inaccuracies tend to be scattered and it is felt that final results are more reliable than those obtained if the ozone were transferred from the HEW cell into some chemical ozone analyzer.

Summary

The peak height, S , at the calibration wavelength of a given pollutant is related to the concentration c within the HEW cell by

$$c = K_{HEW} SA$$

where A is the amplifier attenuation setting. The calibration constant K_{HEW} has units of atmospheres per division and is determined from the slope of the calibration curve such as shown in Figs. 10 through 14. The practical minimum detectable concentration is concluded to be that concentration which produces a five-division peak on attenuation setting of 0.03, i. e., $SA = 0.15$. Smaller attenuation settings are available, but generally result in amplifier overload due to noise. Values of K_{HEW} and c (min) are given in Table 2 for several pollutants.

TABLE 2
D² SYSTEM SENSITIVITIES TO SEVERAL IMPORTANT POLLUTANTS

Pollutant	Peak Wavelength (Å)	K_{HEW}	c (min) Parts per Billion
Nitric Oxide	2269	6.4×10^{-8}	10
Nitrogen Dioxide	2320	5.5×10^{-7}	80
Sulfur Dioxide	2108	1.1×10^{-8}	1
Ammonia	2050	1.2×10^{-8}	2
Ozone	2577	3.0×10^{-7}	45

Field Tests

Field testing was incorporated into the development program of the

air pollution system with the completion of the working hardware. Preliminary objectives were: (1) to test the hardware under field handling conditions so that deficiencies in the design and construction would be revealed, and (2) to obtain derivative spectra of ambient air samples from locations typical to those where such a system would be utilized.

The results of these tests progressively led to the present system as described in this chapter. Minor modifications are still made as field testing continues; but the basic design has been established. Early field test locations were confined to the Gainesville, Florida, area where derivative spectra of air samples near the sewage disposal plant, the power plant, and paper mills were recorded. During these tests, ammonia, sulfur dioxide, nitric oxide, and nitrogen dioxide were detected in the field, and these data were used to establish the required system sensitivities and observe any unexpected background interference. When the final design of the system was established, testing was moved to Jacksonville, Florida, to observe ambient pollution levels in a larger urban center.

The Jacksonville tests, which are summarized here, were conducted primarily during the early rush hours from 7 a.m. to 10 a.m. The system was placed within a station wagon and transported to Jacksonville, where air was continuously drawn into the HEW cell and analyzed for content of several different pollutants, using the automatic wavelength selecting system previously described. Pollutants of prime interest were ozone, nitrogen dioxide, nitric oxide, and sulfur dioxide. These four were often monitored automatically and consecutively so that the concentration of each was recorded at 12-minute intervals. Figures 15 and 16 indicate

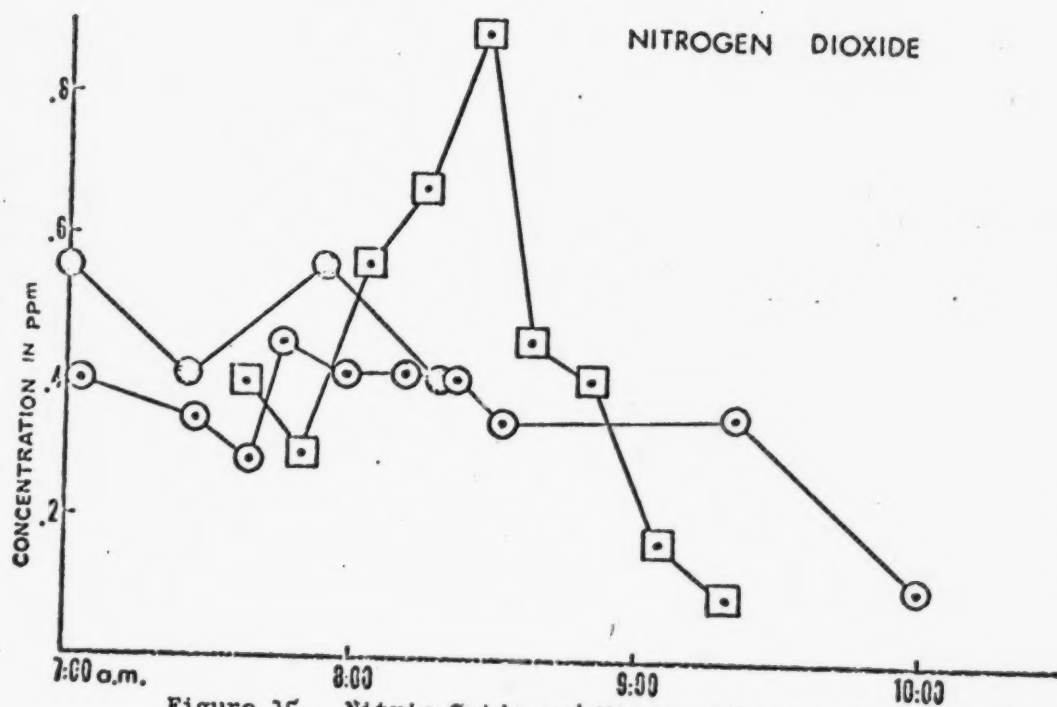
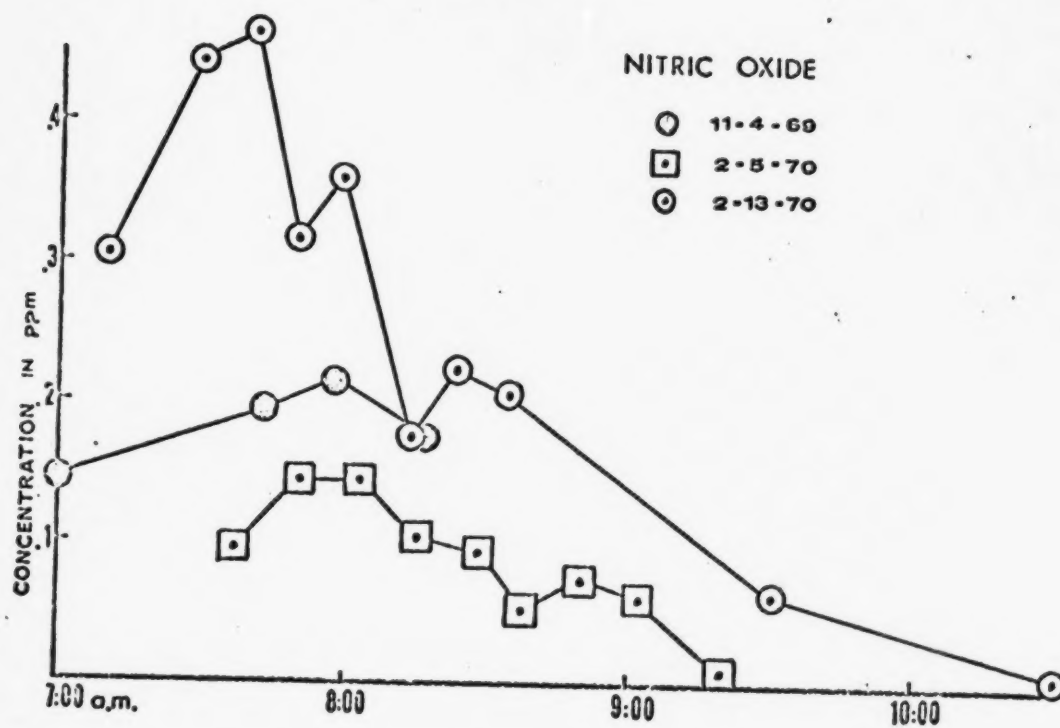


Figure 15. Nitric Oxide and Nitrogen Dioxide Concentrations Measured in Jacksonville, Florida

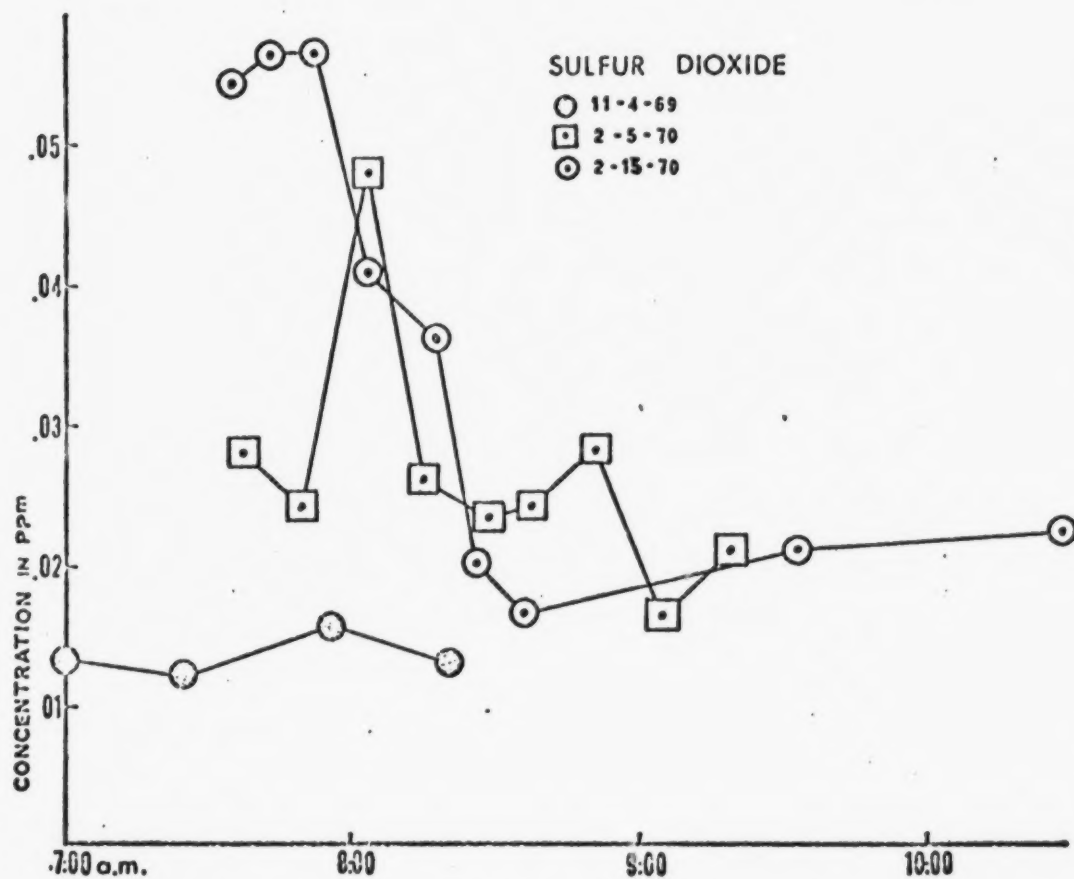
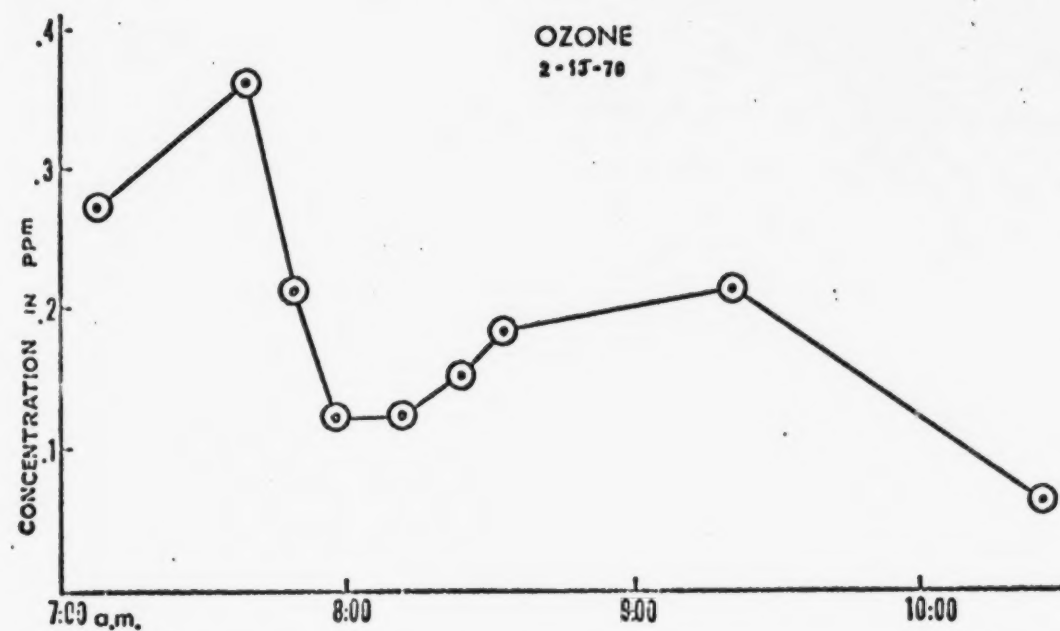


Figure 16. Ozone and Sulfur Dioxide Concentrations Measured in Jacksonville, Florida

typical levels of these pollutants on the dates indicated. It was not the intent of these tests to analyze the variations of concentration with time for the purpose of studying the interactions between the different pollutants--such studies hopefully may be carried out in future research programs. However several features of the data are worth noting.

A maximum in nitric oxide concentration is always noted at the time of peak automobile traffic, between 7:30 and 8:00 a.m.; the concentration thereafter falls to very low values by 10 a.m. Nitrogen dioxide concentration is also reduced considerably by this time, and a prominent maximum is not always detected. The instantaneous concentration of NO_2 is often several times greater than that of NO . The question whether NO is the only source of NO_2 could be determined, in principle, by use of observations with the d^2 spectrometer. The reduction in ozone concentration during the time nitric oxide is disappearing may reflect its role in the oxidation reaction of NO , although firm conclusions of this type are difficult to substantiate with these limited data. There are a number of parameters which can affect instantaneous concentration levels, such as wind speed and direction, solar radiation and humidity, none of which have been precisely considered during periods of data recording thus far. The variations in sulfur dioxide concentration are most probably due to wind speed and direction, since the city power plant is the primary source of the pollutant, at the place where the data here shown were taken, and the concentration measurements were highly dependent upon the location of the effluent plume. The prime objective of these tests was to demonstrate the detectability of the prime urban pollutants under field conditions with the system as it was developed. The objective is concluded to have been achieved.

4. THE d^2 SPECTROMETER APPLIED TO THE MEASUREMENT OF BLOOD AMMONIA

The development of the d^2 spectrometer required a great many tests involving small concentrations of gases which are at best noxious, and at worst highly poisonous. It became a matter of convenience at an early stage to find and use a gas during the earlier developmental work that would have all the salient characteristics of the more common air pollutants, but that would be easily procured, and could be handled outside a hood.

Answering these requirements, ammonia turned out to be ideal. Its spectrum is a series of four bands with satisfactorily high absorption coefficients; it could be obtained readily on campus; in "small" concentrations it could be readily detected by instrument, and was altogether harmless; and in "large" concentrations it could be barely detected by odor. Therefore ammonia was used throughout the program first to develop the instrument, and later to gain experience in its use.

The fact that the detection of ammonia might have interesting aspects quite apart from the area of air pollution was brought to our attention by Dr. J. R. Cade of the J. Hillis Miller Medical Center. Accordingly in a program which became a part of the doctoral dissertation of R. N. Hager, the d^2 spectrometer was applied to the measurement of blood ammonia.

Normal human blood contains a small quantity of ammonia (approximately one microgram per milliliter) in the form of dissolved ammonia gas and ammonium ions. The primary source of this ammonia is the digestion system where it is released during protein fragmentation and absorbed into blood carried by the portal vein to the liver. One of the many things the liver does is to remove most of the ammonia during the six to ten seconds

it takes blood to filter through on the way to the heart.

If the liver begins to function abnormally due to liver disease or cirrhosis, the total ammonia content of the blood increases. Therefore the measurement of a patient's blood ammonia reveals the condition of the liver, and if the liver is diseased, can be used to monitor the progress and response to treatment. Besides being a symptom of liver trouble, an abnormally high blood ammonia level is thought to be the direct cause of the degradation of mental processes which accompany liver disease and lead to the unconscious state termed hepatic coma.

Present Methods of Determining Blood Ammonia

There are many published methods for determining blood ammonia content, but most of them are variations of four general types of analysis. These fall into two general classes: Class I--Removal of ammonia or ammonium ions from the blood and subsequent quantitative analysis, and Class II--Quantitative analysis for ammonia performed directly on the blood.

The microdiffusion process as developed by Conway (14) is of Class I, and is probably the oldest and most generally used method of ammonia determination. Ammonia gas diffuses out of the alkalized blood into an acid. Analysis of the acid represents a point of variation, and can be done by volumetric titration, coulometric titration and colorimetric reaction. The other type of analysis in Class I is the use of ion exchange resins. Plasma ammonium replaces a cation in the resin. The ammonium is converted to soluble ammonia by an alkaline bath; the bath is then analyzed for ammonia content.

In Class II, the most frequently used type is a direct colorimetric

method. There are several variations on an indophenol reaction of deproteinized supernatant described by Okuda and Fujii (15) which results in a color density at 6250 Å proportional to ammonia concentration. The other type of Class II is an enzymatic reaction. The subject is discussed with more references in Ref. 16, in which this work is described.

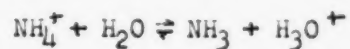
No one type of analysis has been generally accepted or widely used by clinical laboratories. Those methods which seem to give the most reliable results tend to be the most complex to set up and use. This is primarily because, in all cases, the observable is not directly related to the ammonia concentration in the fluid. Instead, a characteristic of some intermediate compound is observed, and the concentration of this compound is related to ammonia concentration. Interference due to substances other than ammonia is a primary source of error, and methods to minimize such errors generally complicate the procedure. Interference effects are more prominent in Class II methods than in Class I methods. However, Class I methods are susceptible to errors from loss and gain of ammonia during the transfer process from the blood to the collecting agent. Minimizing these errors also complicates Class I procedures.

The d² Method for Determining Blood Ammonia

General Description

Since ammonia does not exhibit the absorption band pattern for ultraviolet radiation when dissolved in a polar solvent, it is necessary to detect blood ammonia in the gas phase. Therefore, the first objective of the method is to convert all of the ammonium ions to dissolved ammonia. This can be accomplished by increasing the solution pH.

Total ammonia nitrogen exists in whole blood in the form of ammonium ion and dissolved ammonia gas. The net reaction of these two forms is represented by



The hydrolysis constant is given by

$$K_h = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

where the brackets indicate concentrations.

The ionization constant for ammonia is given by

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

and is equal to 1.8×10^{-5} at 25°C . Since

$$[\text{H}^+][\text{OH}^-] = K_w = 10^{-14}, \quad K_h = K_w/K_b.$$

The ammonia concentration is then related to the total ammonia nitrogen content

$$[\text{A}_m] = [\text{NH}_4^+] + [\text{NH}_3]$$

by

$$[\text{NH}_3] = \frac{[\text{NH}_4^+] K_h}{[\text{H}^+]} = \frac{[\text{A}_m]}{\frac{[\text{H}^+]}{K_h} + 1}$$

or

$$\frac{[\text{NH}_3]}{[\text{A}_m]} = \frac{K_h}{[\text{H}^+] + K_h} = \frac{5.6 \times 10^{-10}}{[\text{H}^+] + 5.6 \times 10^{-10}}$$

For a solution $\text{pH} = 11$, $[\text{H}^+] = 10^{-11}$ and

$$\frac{[\text{NH}_3]}{[\text{Am}]} = \frac{5.6}{5.7} = 0.98$$

and the total ammonia nitrogen is 98 percent ammonia, 2 percent ammonium ion.

Thus the addition to the blood solution of a base can drive essentially all of the ammonium to dissolved ammonia. The ammonia gas dissolved in blood or any fluid will, in a closed vessel, establish an equilibrium with ammonia gas in the vapor state over the fluid. At low concentrations, the equilibrium vapor pressure will be proportional to the concentration of dissolved gas in the fluid in accord with Henry's law.

The method being described utilizes a 10-cm cylindrical quartz cell as the closed vessel. A small measured quantity of de-proteinized blood plasma is added to the cell and there it is thoroughly mixed with a base. The cell is then placed between the exit slit of the d^2 spectrometer and a photomultiplier tube, essentially replacing the HEW cell as described previously. The d^2 instrument records a peak height at the wavelength of an ammonia absorption band maximum which is proportional to the ammonia vapor pressure over the fluid.

At equilibrium, the ratio of the gas to dissolved gas concentrations is a constant. That is

$$\frac{[\text{NH}_3]_G}{[\text{NH}_3]_L} = K$$

where $[\text{NH}_3]_G = P(\text{atm})/24 \times 10^3$ moles per ml at 30°C

and $[\text{NH}_3]_L = W(\text{gm})/17 \times V_L$ moles per ml where V_L is the volume of the fluid.

The total amount of ammonia within the closed cell, in moles, is

$$[A_m] = [NH_3]_G V_G + [NH_3]_L V_L$$

$$= [NH_3]_G V_G \left(1 + \frac{V_L}{V_G K}\right)$$

or
$$[A_m] = P(\text{atm}) \left(\frac{V_G}{24 \times 10^3}\right) \left(1 + \frac{V_L}{V_G K}\right)$$

A typical value for K is 0.002 for the solutions used, and the second term in the parentheses is dominant. If the first term is neglected, it is seen that the vapor pressure, and therefore the d^2 signal, is proportional to the value of K and inversely proportional to the volume of liquid, V_L .

In order to obtain the largest possible signal for a given amount of total ammonia, it is therefore desirable to choose V_L small and also use a base which, in solution, tends to increase the solubility constant K.

The system designed and developed for application to ammonia determination in fluids is shown in Fig. 17. In the figure, the ultraviolet radiation source, a deuterium arc lamp, is shown to the left of the spectrometer. The spectrometer is a basic quarter-meter grating monochromator modified to hold an oscillating entrance slit on the left, and an analyzing section on the right side. Monochromatic radiation exiting the monochromator is rendered parallel and passes through the quartz cell housed within the analyzing section, and is detected by the photomultiplier tube. The electronics and recorder are shown at the right in the photograph.

Protocol

The following protocol was developed for the determination of ammonia nitrogen in blood. The preparation of the whole blood was selected to

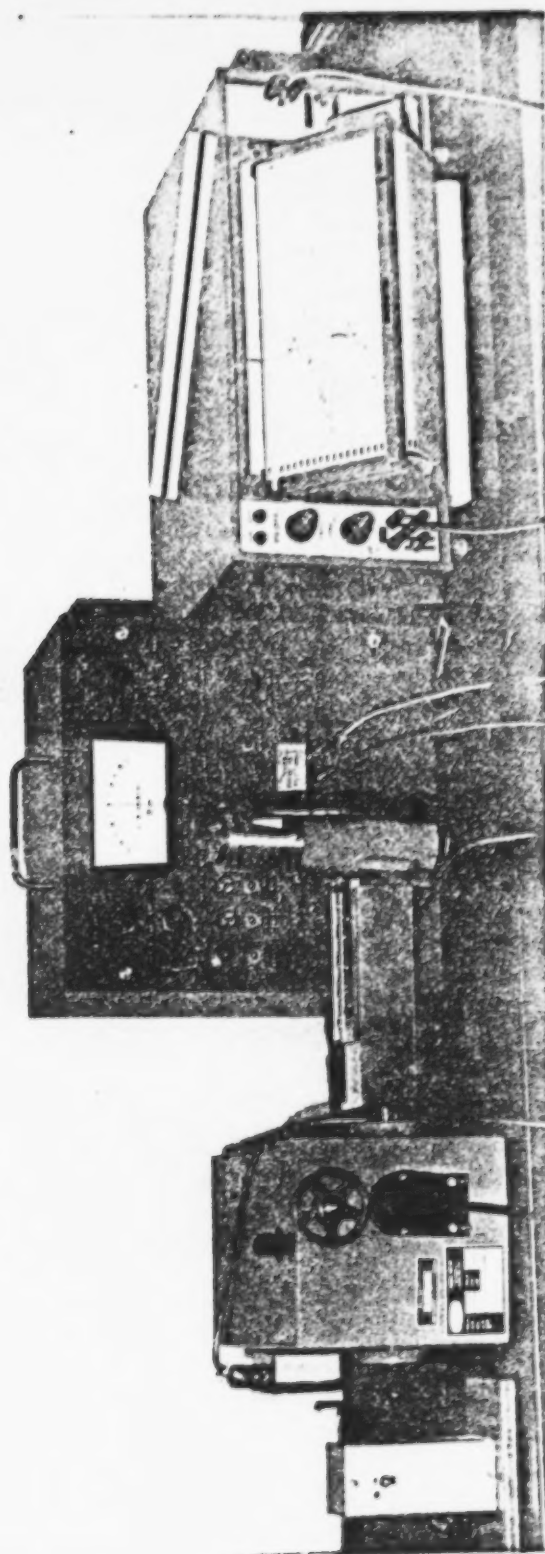


Figure 17. Photograph of the Blood Ammonia Measurement System

parallel those techniques that are most widely accepted.

Five ml of blood is drawn and immediately added to 5 ml of 20% cold (4°C) trichloroacetic acid (TCA). The mixture is vigorously shaken and then centrifuged at 3000 rpm for 10 minutes. The clear supernatant is decanted, covered, and refrigerated at -4°C .

An absorption cell is cleaned with a 50% nitric acid solution, rinsed in ammonia-free water and heated to dryness. Eight-tenths of a gram of solid anhydrous potassium carbonate is added to the cell. One ml of the supernatant is added to the cell and the cell ports are closed. The solution is mixed and all inside surfaces of the cell are wetted. After a background reading on the working range is recorded without the cell in place, the cell is placed in the instrument. The $2050 \text{ \AA}$ absorption band height, h_1 , is recorded several times over a period of 5 to 10 minutes. The cell is then opened and 0.05 ml of a standard ammonium sulfate solution, containing $100 \text{ } \mu\text{g/ml NH}_3$, is added. The $2050 \text{ \AA}$ peak height, h_2 , is again recorded. The ammonium content of the mixture prior to standard addition is computed by the formula:

$$[\text{Am}]_{\text{supernatant}} = \frac{(h_1 - \text{background}) \times 5}{(1.05 h_2 - h_1)} \text{ } \mu\text{g/ml}$$

A blank of the TCA solution is also run; that is, $\frac{1}{2}$ ml ammonia-free water and $\frac{1}{2}$ ml TCA solution is added to a clean cell containing 0.7 g potassium carbonate. The same procedure for determining ammonia content is used for the blank as was used for the supernatant. Finally, the total ammonia contained in one ml of whole blood is:

$$[\text{Am}]_{\text{blood}} = 2 \{ [\text{Am}]_{\text{supernatant}} - [\text{Am}]_{\text{blank}} \}$$

Discussion of the Protocol

The addition of TCA to whole blood is made to precipitate protein which might decompose and alter the ammonia content after shedding, and also to reduce the pH, thus preventing loss of NH_3 during storage. The supernatant is stable for 72 hours without a change in the ammonia level. Heparinized blood can be used and often is, in the Conway microdiffusion technique. It is generally either analyzed immediately after shedding, or quick-frozen and stored at -15 to -25°C . Ammonia content increases rapidly with storage at room temperature but is found to be stable for 4 days at -15°C and 8 days with storage at -20°C . (References in support of these statements are found in Ref. 16).

The addition to the supernatant of potassium carbonate produces two results. First, the pH of the solution is increased to 11.3, so that virtually all the ammonium ions are transformed to ammonia gas. Second, the potassium carbonate ions both act favorably to decrease the solubility of ammonia in the solution through the "salting out" effect.

The signal obtained by use of the derivative spectrometer varies linearly with total ammonia in the fluid as shown in Fig. 18. The calibration procedure is used to establish the slope of the line. Water used in the blank can be checked as to its ammonia content in a manner similar to that used in assaying the supernatant. It was found that tap water contained less ammonia than water obtained from an elaborate pressure distiller ($1.0 \mu\text{g/ml}$ compared to $1.5 \mu\text{g/ml}$). Deionized distilled water contained less than $0.05 \mu\text{g/ml}$. Blanks of TCA and water very seldom showed detectable ammonia.

Multiplying the peak height h_2 by the factor 1.05 in the formula for supernatant ammonia accounts for the slight increase in liquid volume

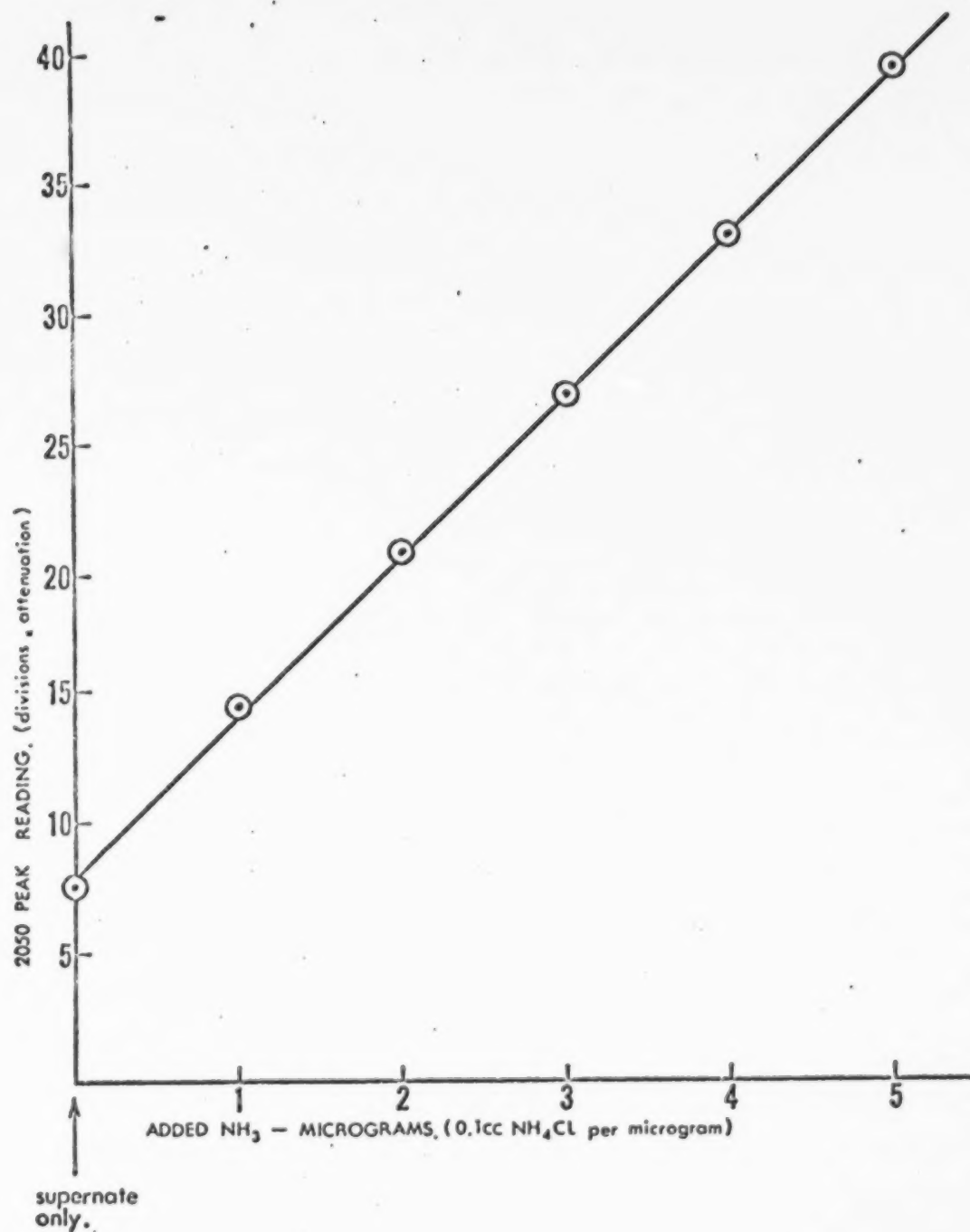


Figure 18. Instrument Readings, as a Function of Added Ammonia

after the addition of the standard. The final figure for whole blood ammonia content is obtained by multiplying the amount determined in the one ml supernatant sample by two. This is the accepted practice; it implies the assumption that the ammonia concentration is distributed evenly throughout the blood solids and the supernatant after centrifugation.

Results of Measurements

Comparison Test

Twenty samples of blood-TCA supernatant were measured for total ammonia content, using the d^2 spectrometric method, and also by a modification of the Conway microdiffusion technique. The results are shown in Fig. 19. The best straight line fit indicates a trend of higher readings with the spectrometric method which would be expected if there were incomplete collection of ammonia during the diffusion process. The mean value of data by the spectrometric method is $2.3 \mu\text{g/ml}$, and that for the microdiffusion data is 2.0 . The slope of the regression line is 0.87 . The standard error of estimate is 0.53 , and the correlation coefficient is 0.75 .

Normal Range

The total ammonia content of blood from 15 normal subjects was measured by the d^2 spectrometric method. The range of measurements was from 0.62 to $1.75 \mu\text{g/ml}$ with a mean of $1.13 \mu\text{g/ml}$. These results are consistent with the clinically accepted normal range of 0.75 to $1.96 \mu\text{g/ml}$.

Abnormal Range

Measurements of blood ammonia content from five abnormal patients were

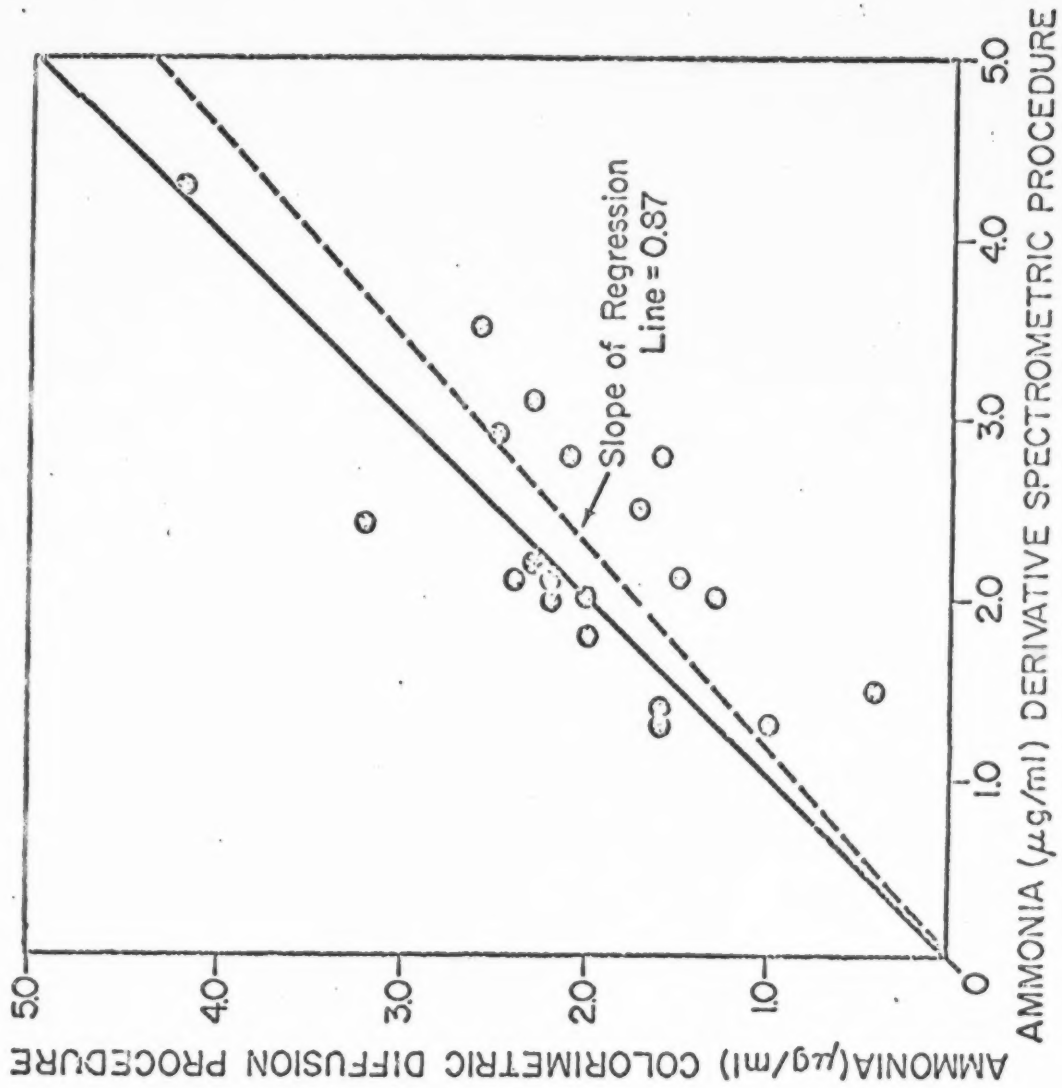


Figure 19. Blood Ammonia Measurements by D² Spectrometric Method Compared to Results by Microdiffusion Method

made using the d^2 spectrometric method. These measurements were made upon request of physicians connected with the J. Hillis Miller Health Center and the Veterans Administration Hospital. The results are shown in Table 3. All values exceeded the normal range previously established.

TABLE 3
BLOOD AMMONIA MEASUREMENTS FROM ABNORMAL SUBJECTS

Subject	Total Blood NH_3 ($\mu g/ml$)	Condition
1	2.2	Liver disease
2	4.6	In hepatic coma
2	2.1	Out of coma
3	3.1	Liver disease-disoriented
3	1.8	1 day later, oriented
3	2.2	1 day later, oriented
4	2.7	Liver disease
5	6.4	Liver disease-critical

Repeatability of Measurements

Thirty-five independent samples of supernatant were measured twice for ammonia content by the d^2 spectrometric method. The mean value for each sample was determined. The average deviation from this mean was 6.1% with a standard deviation of 3.8% from the average deviation.

Storability of Supernatant

Results of measurements made on the same sample of supernatant after periods of storage at $-4^\circ C$ indicate values remain within the average scat-

ter range for storage periods up to 72 hours. Data in Table 4 show increases outside the 6.1% range for storage times greater than 72 hours. Samples 1, 2 and 3 are 16%, 22%, and 16% high, respectively, at 96 hours.

TABLE 4
BLOOD AMMONIA MEASUREMENTS OF STORED SUPERNATANT

Sample	Blood NH_3 ($\mu\text{g/ml}$)	Comment
1	1.54	Normal subject, immediate analysis
1	1.62	Stored @ -4°C for 72 hours
1	1.84	Stored @ -4°C for 96 hours
2	0.82	Normal subject, immediate analysis
2	1.10	Stored @ -4°C for 96 hours
3	1.13	Normal subject, immediate analysis
3	1.34	Stored @ -4°C for 96 hours
3	1.38	Stored @ -4°C for 120 hours
4	2.06	Abnormal subject, immediate analysis
4	2.48	Stored @ -4°C for 120 hours

Conclusions

The data, as reported, justify the conclusions that the d^2 spectrometric method can be used for the accurate determination of blood ammonia. The results of the comparison test indicate a predictable trend for this method compared to the microdiffusion method. The normal range was established to be within the accepted values and abnormal blood content was clearly revealed. Consistency in duplicate readings was not found to be exceptional, but the amplitude of variation could probably be reduced by efforts to reduce pipetting errors, especially during the addition of the 0.05 ml standard solution.

The advantages inherent in this method are the simplicity in procedure as compared with chemical methods, the direct detection of ammonia rather than an intermediate, and the lack of interference. A consideration of major importance in assessing the value of this or any other new method of ammonia measurement is whether the new method is free of interference--whether it can possibly measure some material other than ammonia, and yield, therefore, a false datum. It is a fundamental fact that the spectrometric method described here cannot in the nature of things yield a result in error because of interference by some other material than ammonia, without the knowledge of the spectroscopist.

The four peaks shown in Fig. 6 represent a part of the ultraviolet absorption spectrum of ammonia. The wavelength at which the peaks occur and their relative intensities are uniquely characteristic of ammonia gas. No other compound exhibits exactly this pattern. Other compounds can exhibit absorption peaks in the neighborhood of the ammonia peaks, which can affect the observed peak heights of ammonia, but such occurrences are immediately

detectable, since the ammonia absorption pattern will be distorted by that of the interfering compound.

It is worth noting that during all the tests, there was never any distortion of the ammonia spectrum by compounds within the blood-TCA supernatant. In one case, spectral interference was observed in both the blank and the sample, and the interfering compound was traced to contamination within a supply of factory-sealed test tubes.

SUMMARY

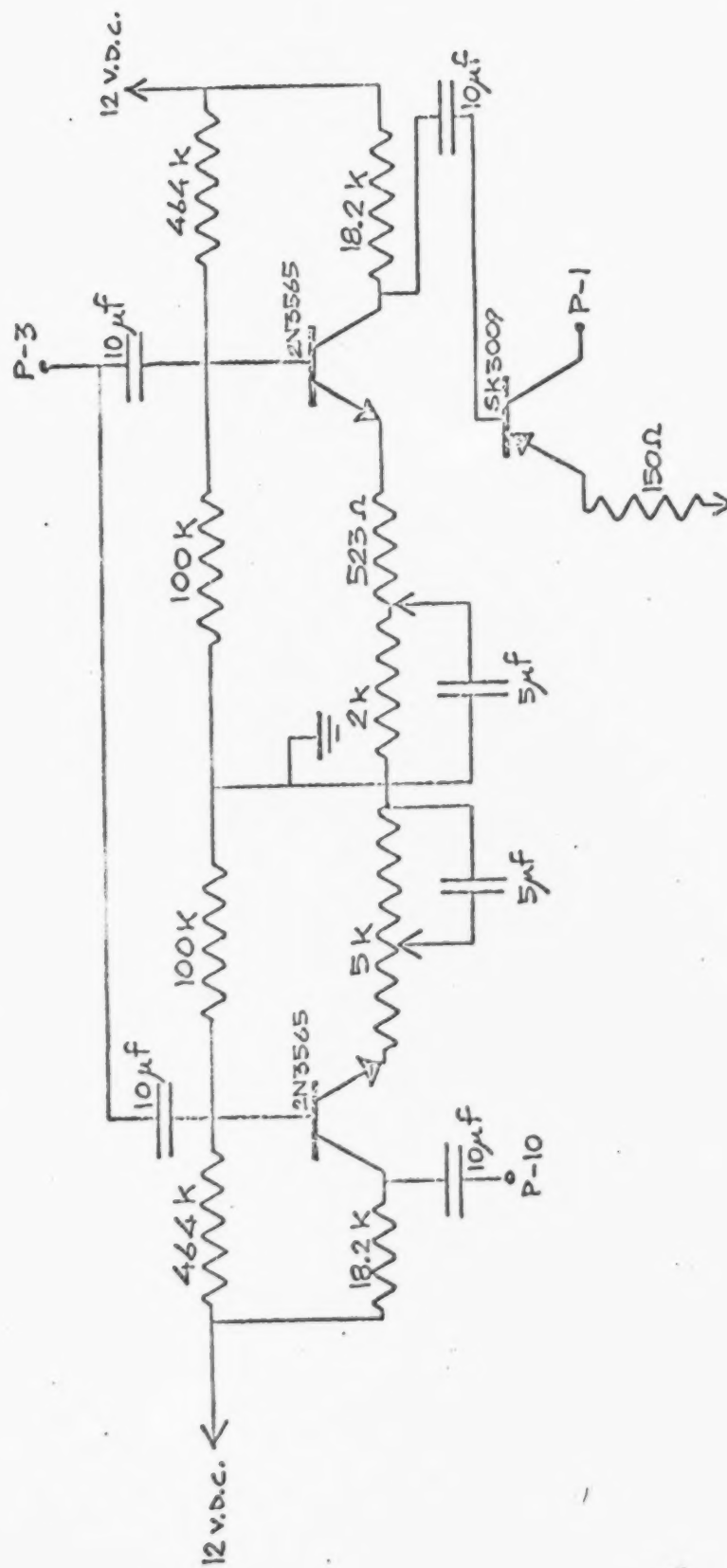
The second derivative spectrometer has been shown to provide a substantially improved sensitivity to small concentrations of gases as compared to a conventional spectrometer. This advantage is due to the use of the wobbler coupled with the potentiometric recorder. Applications to fields other than air pollution detection are readily conceivable, beyond the medical application already investigated. Such applications merit exploration, though there is no immediate requirement on the part of HEW to promote such studies.

A direction in which further extension of the d^2 principle might be of advantage in air pollution detection is an extension to the infrared. There are known pollutant gases, such as CO and H_2S , that are not now detectable spectrometrically by use of the visible or ultraviolet instruments, that would probably be detectable by use of an infrared version. A proposal of such an extension has been made, and it is possible that the program will get under way in 1971. It should be kept in mind that the use of a chopped signal, fundamental to the d^2 instrument, is already employed in infrared spectrometers. On that account, it is possible that

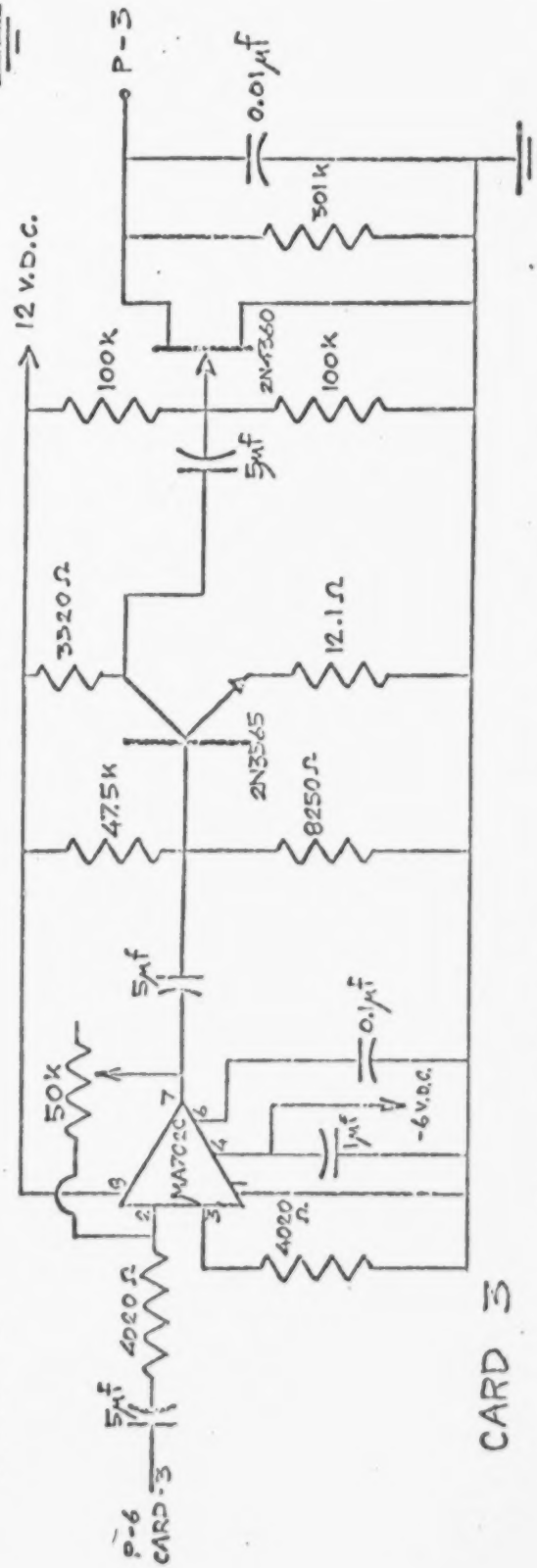
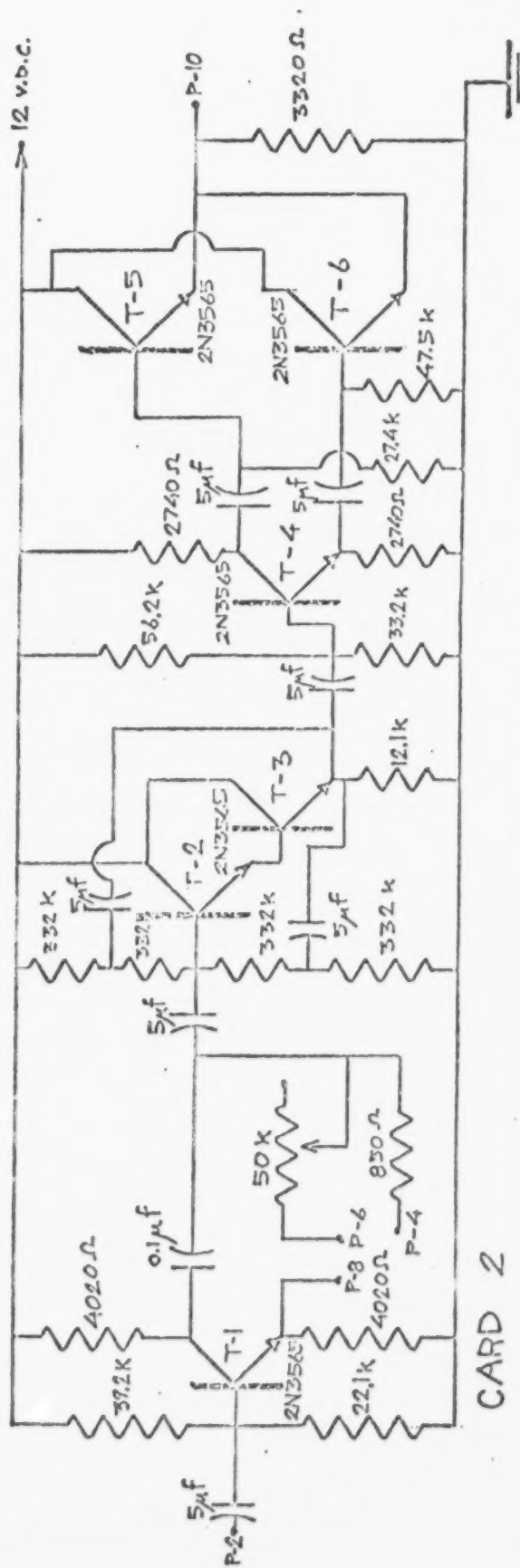
the infrared version of the d^2 spectrometer may not demonstrate as sensational an improvement in capability over current spectrometric practice as was the case in the uv and visible.

A realistic view of the future of the d^2 spectrometer is that its application to air pollution measurement is already demonstrated. It should be put into practice as soon and as extensively as possible, so that the government and the public may profit from the development as funded. Further improvements in instrumentation are to be anticipated assuming the instrument can be made to sell for a profit, and assuming a suitable market develops over the course of the next few years.

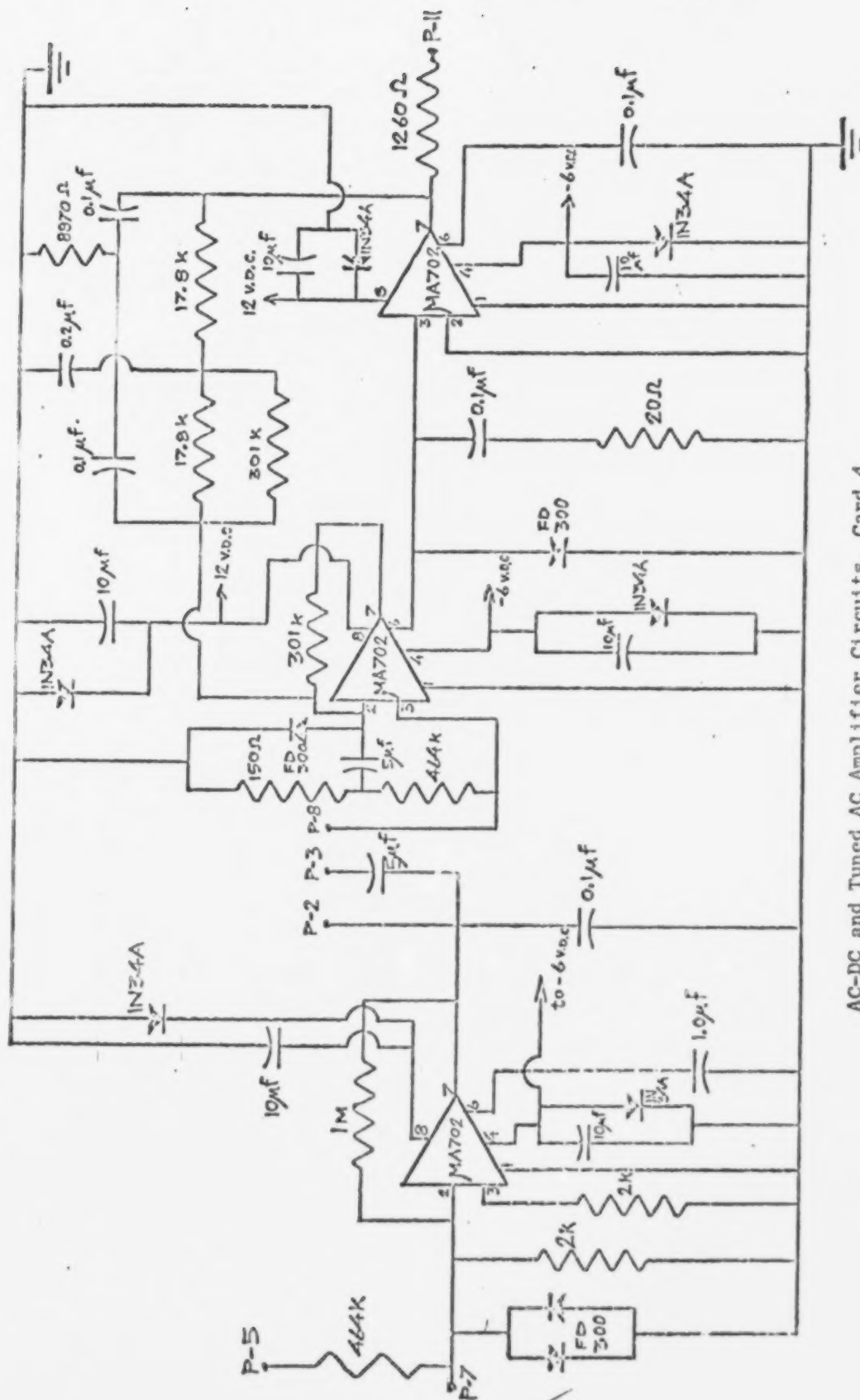
APPENDIX A



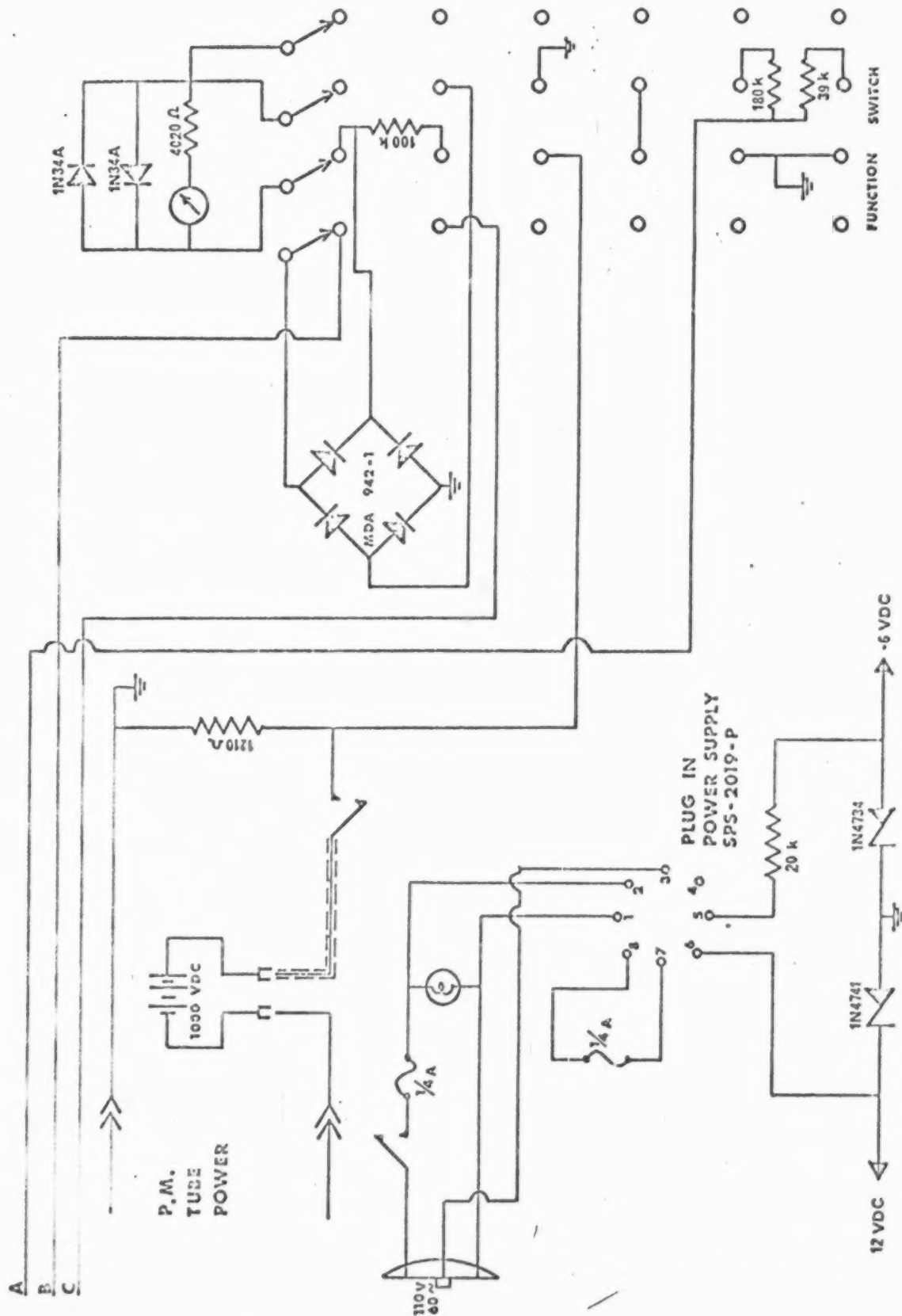
Wobbler Driving Circuit, Card 1



Reference Signal Conditioning Circuit, Cards 2 and 3



AC-DC and Tuned AC Amplifier Circuits, Card 4



D² Instrument Circuit Diagram, 2 of 2

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